JOURNAL
OF THE
WASHINGTON ACADEMY OF SCIENCES

VOL. 45 October 1955 No. 10

PHYSICAL CHEMISTRY.—*Tritium in nature*[1]. W. F. LIBBY, U. S. Atomic Energy Commission. (Communicated by R. K. Cook.)

(Received July 29, 1955)

I. INTRODUCTION

Among the products of the collisions of the cosmic rays with the atmosphere which one might expect to find in detectable quantities in nature is tritium, radioactive hydrogen of mass 3, 12.5 half life, 18 years average life, which disintegrates to form the stable isotope of helium of mass 3. Tritium had been sought in natural waters prior to the discovery of its natural radioactivity. The methods used in this early search were inappropriate since they assumed that tritium would be a stable isotope and were not of sufficient sensitivity to detect natural tritium. It was fortunate, however, that the samples prepared for this original search of Lord Rutherford[2] and his colleagues at the Cavendish Laboratory were available for the search for radioactive tritium. It had been shown from earlier researches[3] that the bombardment of nitrogen by fast neutrons of energies above 5 million volts produced tritium and the cross section for this reaction was such that the neutrons which had been observed by Korff[4] to be formed by the bombardment of the atmosphere by cosmic rays would produce tritium in sufficient yield to cause one to expect it to be observable.[5] It was speculated at the time that the amount of tritium produced in this manner could easily explain the extraordinary abundance of helium 3 in atmospheric helium. Helium 3 in atmospheric helium is about 1 part per million of the total helium, whereas in well or terrestrial helium it is only one-tenth as abundant as in atmospheric. Therefore, we understand that the helium 3 in atmospheric helium is of cosmic ray origin, probably.

There is reason to believe that tritium produced by the cosmic rays would be produced in the high levels of the atmosphere, probably above the tropopause, between 30 and 50 thousand feet on the average. It, of course, could be produced at all levels to some extent though it would be most abundantly produced at the highest levels. We further expect that there would be opportunity for most of the tritium atoms formed to burn to form water and consequently that the water of the atmosphere should be radioactive with tritium. An analogous research undertaken in Germany[6] at about the same time as our first work showed that the tritium might have some difficulty burning to form water by showing that atmospheric hydrogen is especially rich in tritium as compared to atmospheric water, it being about 10,000 times more concentrated. However, it is still true that over 99 percent of the tritium burns to form water since the atmospheric hydrogen is so extremely rare relative to the moisture of the atmosphere.

The Rutherford sample was obtained by Dr. A. V. Grosse and was electrolyzed and converted into deuterium gas, after which the deuterium gas was placed inside a geiger counter. It is necessary to count tritium in

[1] The Twenty-fourth Joseph Henry Lecture of the Philosophical Society of Washington, delivered before the Society on March 25, 1955.
[2] Lord RUTHERFORD, Nature **140**: 303. 1937.
[3] CORNOG, R., and LIBBY, W. F., Phys. Rev. **59**: 1046. 1941.
[4] Rev. Mod. Phys. **11**: 211. 1939.
[5] LIBBY, W. F., Phys. Rev. **69**: 671. 1946.
[6] FALTINGS, V., and HARTECK, P., Zeit. Naturforsch. **5A**: 438. 1950.

the internal volume of a geiger counter for the reason that its radiation is so extremely soft, 19 kilovolt energy upper limit to the beta spectrum. Because of this softness it will not penetrate with any reasonable efficiency through a wall of any finite thickness nor emerge from a solid sample. The deuterium gas obtained by electrolysis and reaction of the heavy water produced with hot zinc metal was mixed with a small proportion of ethylene gas (1 or 2 cm of mercury pressure) and a small amount of argon (about 3 cm mercury pressure). This counting gas is a good geiger counter mixture and performs very well. The counter was shielded by standard anticoincidence techniques and by a thick metal shield.[7] The geiger counter had a natural background of about five counts per minute when so shielded though the volume was nearly eight-tenths of a litre. The electrolyzed heavy water sample produced for Lord Rutherford at an extreme enrichment of any tritium present of nearly ten million fold showed a very appreciable radioactivity. In fact, the radioactivity was so strong that it was several weeks before the failure of the counter to operate in a reliable fashion was understood by diluting the deuterium samples with ordinary hydrogen gas and observing that the cause of the troubles was the excessive radioactivity of the deuterium gas from the Rutherford sample. The sample had been prepared by the Norsk Hydro heavy water concern by electrolyzing heavy water to further concentrate any tritium which might have been present in the original water used to make the heavy water. The original water used to make the heavy water in the Rutherford sample came from the Lake Mösvan, which lies on the mountain plateau just east of Bergen in Norway. It was therefore quite certain that the water electrolyzed to form the Rutherford sample was fresh snow water and therefore had not had an opportunity to lose its tritium by radioactive decay. Dr. Grosse, Dr. Wolfgang, Dr. Johnston, and I all worried that the excessive radioactivity found in Rutherford's sample might be inadvertent in that in 1936 when the sample prepared for Lord Rutherford's search for tritium in nature had been studied in the Cavendish Laboratory heavy water was quite a rare commodity and it might have been used in the deuteron accelerator. Tritium is produced in prolific quantities by the reaction between deuterons and this tritium would have easily explained our observations. We therefore asked the Norsk Hydro Company to prepare a duplicate of the Rutherford sample. This was done, and it completely confirmed the assay found in the Rutherford sample. The abundance of tritium[8] using modern values[9] for the fractionation factor of the Norsk Hydro plant was 2.4×10^{-18} atoms of tritium per atom of ordinary hydrogen, a value close to that expected.[5] As a result of the discovery that rain and snow do, indeed, contain tritium in about the concentration expected, it was decided to pursue the assay of the natural waters of the earth for cosmic ray tritium and to study its possible practical useful applications.

[7] ANDERSON, E. C., ARNOLD, J. R., and LIBBY, W. F., Rev. Sci. Instr. **22:** 225. 1951.

II. METHOD OF MEASUREMENT

The water sample to be assayed for tritium content is first distilled in a standard 2-gallon gas-fired still, then is mixed with sodium hydroxide to produce a 3-percent (by weight) solution, and finally is electrolyzed in an iron-nickel anode plant[10] to a volume of about 1 cc or less and the deuterium and tritium content of the final product determined. It has been observed that the ratio of the separation factors for tritium and deuterium can be taken as 2.0 within the experimental error of the data which is about 5 percent.[11] This results in the very simple expression,

$$\frac{T}{T_0} = \sqrt{\frac{N \times V_0}{N_0 \times V}}$$

In this equation T and T_0 are the final and original concentration of tritium respec-

[8] GROSSE, A. V., JOHNSTON, W. H., WOLFGANG, R. L., and LIBBY, W. F. Science **113:** 1. 1951. Material in this article was presented at the First Research Day of Temple University's Research Institute, September 14, 1950.

[9] HARTECK, P., private communication.

[10] BROWN, W. G., and DAGGETT, A. F. Journ. Chem. Phys. **3:** 216. 1935.

[11] KAUFFMAN, S., and LIBBY, W. F. Phys. Rev. **93:** 1337. 1954.

tively in the water samples. N is the final concentration of deuterium and N_0 is the initial concentration of deuterium which is[12] 0.0156 percent for ocean water, Chicago rain, 0.0149 percent, Chicago snow, 0.0141 percent.[13] If one takes the original volume of water to be 10–20 liters in the case of rains and rivers and 100 liters in the case of ocean water and the final volume to be 0.3 to 0.5 cc.[2] the resulting concentration of tritium, τ, is adequate to allow several counts per minute of observable count rate above the background of about four counts per minute. With this arrangement it has been possible to complete a considerable number of assays for natural tritium.[14] The general result has been that the average tritium production rate by the cosmic rays is about 0.14 tritium atoms per cm^2 per second of the earth's surface, with a probable error of about 20 percent of this number. This is a very large yield considering that the intensity of the cosmic rays themselves is somewhere between 0.5 and 1 primary particle per cm^2 per second. In other words, between one-third and one-seventh of all the primary radiations hitting the earth succeed in producing a tritium atom. These high yields are being confirmed in studies in progress with Lloyd Currie, Dr. R. L. Wolfgang, and Dr. M. L. Kalkstein in progress at the present time at the Brookhaven Cosmotron which furnishes 2.05 billion volt protons and at the Berkeley Bevatron which furnishes 5.7 billion volt protons. The cross sections for the production of tritium for a wide range of targets encompassing the range of elements have been large. In fact, as an average result one finds that about one-tenth of all the collisions in this billion volt energy range produces tritium. This is a large yield considering the small binding energy which tritium has and the essential instability of this particle. However, it does indicate that the cosmic-ray production rate given by the study of the tritium in the waters of the earth is essentially correct. The assay results are given in Table 1.

[12] CRAIG, HARMON, private communication.
[13] Figures quoted in earlier publication[14] were incorrect. Numbers given here are the correct numbers.
[14] VONBUTTLAR, H., and LIBBY, W. F., Journ. Inorg. and Nuclear Chem. **1**: 75. 1955.

III. TABLE 1

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
	A. *Chicago Rains and Snows*	
5	May 11, 1951. Collected from 1000 to 1200. Storm lasted from evening of 10th to afternoon of 11th. 3.81 in. rain.	33 ± 2
14	October 14, 1952. Collected throughout storm. Storm lasted from 1700 to 2400. 0.70 in. rain.	20.4 ± 0.7
16	November 17, 1952. Collected throughout storm. Storm lasted from 0030 to 0100; 0600 to 0630. 0.31 in. rain.	37 ± 3
17	November 18, 1952. Collected throughout storm. Storm lasted from 2100 of 17th to 1200 of 18th. 0.70 in. rain.	66.0 ± 1.0
18	November 22–24–25, 1952. Collected throughout storms. Rained afternoon of 22nd, evening of 24th, all day 25th. 1.13 in. rain.	19.3 ± 1.5
19	December 2, 1952. Fell during night. 0.29 in. snow.	13.2 ± 1.2
21	January 6, 1953. Fell during afternoon. 0.05 in. snow.	7.1 ± 0.5
22	January 23, 1953. Collected from 1515 to 1530. Storm lasted from 1200 to 1900. 0.32 in. rain.	9.0 ± 1.0
30	February 11, 1953. Collected from 0930 to 1245. Light rain all morning. 0.03 in. rain.	5.0 ± 0.7
33	February 16, 1953. Collected 1030. Fell from 0300 to 1400. 0.19 in. snow.	10.8 ± 1.0
34	February 20, 1953. Collected 1615. Storm lasted from 1530 to 1645. 0.94 in. rain.	3.3 ± 0.3
38	March 3, 1953. Collected throughout storm. Rain, sleet, and snow fell from 1300 to 2000. 0.38 in. rain.	9.4 ± 1.0

TABLE 1 (*Continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
39	March 7, 1953. Collected 1200. Fell from 0800 to 1500. 0.18 in. snow.	9.6 ± 0.8
40	March 12, 1953. Collected 1030. Storm lasted from 0900 to 1700. 0.98 in. rain.	4.75 ± 0.20
45	March 14, 1953. Collected throughout storm. Rained from 1000 to 1600; 2000 to 2200. 1.05 in. rain.	1.16 ± 0.18
46	March 18, 1953. Collected throughout storm. Light rain from 1300 to 1700. 0.13 in. rain.	7.9 ± 0.3
48	March 21–22, 1953. Collected throughout storms. Rained night of 21st, night of 22nd. 0.06 in. rain.	3.10 ± 0.13
50	March 31, 1953. Collected from 1030 to 1100. Rained lightly from 1000 to 1200. 0.07 in. rain. Wtd. Ave. (December to March):	9.5 ± 0.4 5.5
51	April 3, 1953. Collected from 1000 to 1200. 0.07 in. rain.	9.1 ± 0.3
56	April 15, 1953. Collected from heavy rain 1130. 0.60 in. rain.	10.0 ± 0.3
61	April 30, 1953. Rained heavily from 1830 to 1915 with thunder and lightning. 0.87 in. rain.	6.6 ± 0.4
67	May 22, 1953. Collected at 0945. Heavy thunderstorm. 0.82 in. rain.	6.7 ± 0.3
74	June 5, 1953. Collected from 1530 to 1610. Thunderstorm. 0.43 in, rain.	6.2 ± 0.2
76	June 25, 1953. Collected from intermittent rain between 2130 and 2400. 0.02 in. rain.	7.9 ± 0.1
77	July 1–2, 1953. Collected between 2300 on July 1 and 0300 on July 2. Trace rain on July 1, 0.06 in. on July 2.	4.3 ± 0.3
79	July 5, 1953. Collected from July 3 to July 6. Storm occurred about 2200 on July 5. 0.39 in. rain.	7.6 ± 1.5
86	July 17–20, 1953. Collected from 0930 July 17 to 1600 July 20. Rainstorms on morning of July 17, afternoon of July 17, night of July 18, and morning of July 20. Rainfalls were; 0.57 in. July 17; trace July 18; 0.10 in. July 20.	7.1 ± 0.4
91	August 3, 1953. Collected 1930 to 1945. Trace rain.	3.60 ± 0.4
92	August 4, 1953. Collected 1445 to 1455. 0.06 in. rain.	17.0 ± 0.4
96	September 4, 1953. Collected 0400 to 1100. 0.50 in. rain. This was the first rain after 3 weeks drought.	7.3 ± 0.6
97	September 18, 1953. Rained very hard—thunderstorm. Collected at 2145. 0.63 in. rain.	12.0 ± 0.4
101	October 18, 1953. Trace rain.	9.8 ± 0.9
102	October 26, 1953. First drops collected. Total rainfall was 0.31 in., but this sample consisted of the first drops. Collected at 1530.	19.9 ± 1.0
103	October 26, 1953. Same storm as sample No. 102 except water collected after three hours of continuous rain. Collected at 1800. 0.31 in. rain.	20.0 ± 1.0
106	November 20, 1953, Collected 9000 to 1100 from the first part of the rainstorm. 0.56 in. rain.	7.3 ± 0.9
107	November 20, 1953. Collected 1600 at end of rainstorm.	13.5 ± 1
109	November 27, 1953. Collected in the morning after an overnight snow.	34.5 ± 0.6
132	December 2, 1953. Rain. Collected at 1500.	7.85 ± 0.25
134	December 2, 1953. Rain. Collected at 1700.	8.3 ± 0.3
135	December 3, 1953. Rain. Collected from 0925 to 0930.	5.8 ± 0.4
142	December 12, 1953. Rain.	7.8 ± 0.3
136	January 20, 1954. Rain. Collected from 0845 to 0855.	10.5 ± 0.3
137	January 21, 1954. Snow. Collected at 1700.	18.7 ± 0.4
138	January 26, 1954. Rain. Collected from 1000 to 1400.	19.4 ± 0.5
139	February 5, 1954. Rain and Snow. Collected after 1700.	23.0 ± 1.5
140	February 15, 1954. Heavy rain with thunder and lightning. Collected from 1900 to 2200.	9.5 ± 0.4
141	February 16, 1954. Snowy rain. Collected from 1500 to 1600.	15.6 ± 0.7
147	March 2, 1954. Snow fell 1500 to 2400. Shoveled from the ground on March 3, 1954 at 1430.	20.8 ± 0.5
151	February 20, 1954. Rain. Collected from 1230 to 1315.	4.2 ± 0.2
166	March 19, 1954. Rain. Collected from 1430 to 1540.	385 ± 5

TABLE 1 (*Continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
167	March 24–25, 1954. Rain.	283 ± 3
168	March 29, 1954. Fresh snow.	196 ± 3
169	March 29, 1954. Collected March 31, 1954, after most of snow had melted.	145 ± 5
170	April 7, 1954. Heavy shower. Collected 1530.	248 ± 5
171	April 15, 1954. Short, heavy storm. Rain. Collected 1130–1145.	360 ± 6
174	April 19, 1954. Collected at 1745. It had been raining since about noon.	425 ± 20
175	April 20, 1954. Collected at 0900 during rain on April 21, 1954.	260 ± 4
181	May 26–27, 1954. Collected during rainfall at night.	450 ± 10
182	May 27, 1954. Collected at 1105–1110. Different rainstorm from sample No. 181.	416 ± 15
183	June 1, 1954. Collected 0930–0935. Rained previous night and all day.	390 ± 5
	Average tritium content from December 1, 1952 to December 1, 1953 weighted according to the total rainfall for storm samples for 27 samples amounting to 12 inches out of the total rainfall of 26 inches.	8.2
	Unweighted average for the samples between December 1, 1952, and December 1, 1953.	7.8
	Calculated average for rainfall over the past 18 years (Lake Michigan).	7.4
	B. *Rains and Snows from Other Areas*	
42	Fayetteville, Arkansas, snow. January 23, 1953. 1.17 in. snow.	5.5 ± 0.6
43	Wilson Springs, Arkansas, rain. Collected on February 10, 1953 in a heavy thunderstorm.	2.25 ± 0.8
49	Honolulu, Hawaii, rain. Collected on morning of March 26, 1953 at Honolulu, 5329 Keikilani Circle by Mrs. Terry Yoshida.	0.61 ± 0.10
95	Hickham Field, Oahu, Hawaii, rain. Collected at Hickham Field, July 17, 1953.	0.59 ± 0.08
98	Manila, Philippine Islands, rain. Collected 5 June, 1953 at the Bureau of Quarantine by Dr. R. Abriol.	0.90 ± 0.07
110	Tantalus, Koolau Range, Oahu, Hawaii, rain. Collected 13 November 1953. The rain was collected by residents of Tantalus.	0.73 ± 0.11
120	Oahu, Hawaii, rain. Collected by pooling the catches of several rain gages located at: Lower Laukaka, Nuuahu Reservoir No. 4, Wil. Rise No. 4, Manoa Valley, Palolo Valley, Nuuahu Pali, Kalihi, U.S.G.S. Station, Kaliha, Tunnel No. 2, Kaliha Reservoir Site, Tantalus Peak, Bureau of Water Supply, City and County of Honolulu.	0.67 ± 0.14
121	Manoa Valley, Hawaii, rain. December 1953. Single rain.	1.53 ± 0.11
125	Wellington, New Zealand, rain. Collected October 1, 1953 on the roof of the American Embassy at Wellington, New Zealand. The roof had recently been painted and consisted of galvanized iron. The meteorology: a vigorous depression was located at the Tasman Sea west of Cook's Strait. It moved ESE and came over Wellington in the early hours of October 2, 1953. Rainfall from the forward side of the depression began when the cloud base was at 3 kilometres. After it began to rain the cloud base moved down to 1 to 2 kilometres and the freezing level was at 2 kilometres. The clouds were alto stratus and nimbo stratus.	1.7 ± 0.2
126	Harwell, England, rain. Two gallons collected after a windless week on October 24–25, 1953. Artificial tritium from Harwell may have been present in this sample. Sample sent by J. M. Fletcher.	22.5 ± 0.6
127	Harwell, England, rain. Collected October 26 to 28, 1953. Artificial tritium from Harwell may have been present in this sample.	25.5 ± 0.4
128	Santa Barbara, California, rain. Rain fell on January 23 and January 24, 1954. Collected by Dr. V. L. Vanderhoof on January 24, 1954 from Mission Creek, Santa Barbara. Total rainfall was 3 inches.	4.0 ± 0.1

TABLE 1 (*Continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
164	Kobe, Japan, rains. November, 1953 (4 or 5 storms). Sent by Prof. Seishi Kikuchi, Osaka University.	6.5 ± 0.4
165	Puerto Rico, rain. March 26, 1954. Drained off a tin roof at Ramez Air Force Base. Total rainfall 0.42 inches.	65.6 ± 1.2
179	Valparaiso, Chile, rain. April 4 or 5, 1954. After 3 months' drought. Rained very heavily for about 36 hours.	4.3 ± 0.2
	Water from Lake Mösvan used to supply the Norsk-Hydro. The Lake Mösvan water probably was melted snow from the winter of 1946 and 1947. The water was taken from the lake at the end of January, 1948. (8)	2.4
	C. *Mississippi River*	
23	Mississippi River, St. Louis, January 31, 1953.	5.6 ± 0.6
24	Mississippi River, Rock Island, January 29, 1953.	2.5 ± 0.3
26	Mississippi River, St. Louis, February 4, 1953.	4.5 ± 0.6
27	Mississippi River, Rock Island, February 6, 1953.	3.7 ± 0.4
28	Mississippi River, Memphis, February 4, 1953.	6.0 ± 1.0
29	Mississippi River, New Orleans, February 8, 1953.	4.7 ± 0.3
31	Mississippi River, St. Louis, February 10, 1953.	6.0 ± 0.9
36	Mississippi River, St. Louis, February 20, 1953.	6.4 ± 0.5
37	Mississippi River, Rock Island, February 24, 1953.	4.4 ± 0.2
44	Mississippi River water from Rock Island. Collected March 16, 1953.	3.2 ± 0.2
47	Mississippi River water from St. Louis. Collected 0900 on March 17, 1953.	5.4 ± 2.4
57	Mississippi River water from Rock Island. Collected 1315 on April 17, 1953.	5.3 ± 0.3
58	Mississippi River water from St. Louis. Collected 1300 on April 17, 1953.	6.0 ± 0.4
80	Mississippi River water from Rock Island. Collected on June 30, 1953.	7.2 ± 0.7
88	Mississippi River water from St. Louis. Collected 1320 on July 22, 1953.	7.3 ± 0.4
	Average for Rock Island	4.7
	Average for St. Louis	6.0
	D. *Other Rivers*	
10	Columbia University distilled water. Collected August 5, 1944.	2.4 ± 0.1 (4.5 ± 0.2 as of 1953)
15	Sangamon River, Decatur, August 6, 1952.	1.15 ± 0.08
52	Arkansas River, Conway, Arkansas, March 20, 1953.	3.12 ± 0.10
104	Riber Elbe. Collected at Hamburg, Germany, on August 31, 1953.	2.57 ± 0.12
105	River Weser. Collected at Bremen on September 1, 1953.	1.76 ± 0.10
108	River Rhone. Collected near Lyon, France, on September 10, 1953.	2.64 ± 0.16
111	River Main near Würzburg, Germany. September 13, 1953. Collected by Dr. H. V. Buttlar, who collected all the European samples.	1.76 ± 0.19
112	River Loire. Collected at Digoin, France, on September 9, 1953.	2.11 ± 0.14
114	English stream near river Cam. Water taken about one mile from the source (a spring). Collected near Cambridge, England.	1.25 ± 0.10
122	River Donau. Collected near Ulm, Germany, on September 12, 1953.	2.13 ± 0.38
123	River Mosel. Collected near Metz on September 7, 1953.	2.15 ± 0.12
124	River Seine. Collected near Nogent, France, on September 8, 1953.	1.80 ± 0.3
131	River Fulda. Collected near Kassel on September 24, 1953.	2.35 ± 0.1
132	River Rhine. Collected between Geisenheim and Rüdesheim on September 7, 1953.	3.0 ± 0.3
133	River Marne at Joinville, collected September 8, 1953.	2.1 ± 0.2
143	Shasta Dam, California. January 30, 1954.	2.7 ± 0.1

TABLE 1 (*Continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
144	El Rito de los Frijoles, Jemez Mountains, New Mexico. Collected February 7, 1954, at Bandelier National Monument. Sample probably represents average over the winter snowfall in the Jamez Mountains. Sent by E. C. Anderson.	27.2 ± 0.4
145	Rio Grande, northwest of Santa Fe, February 7, 1954. The spring thaw was beginning to raise the river level, but it had not yet reached peak volume by any means. Sent by E. C. Anderson.	6.6 ± 0.2
146	Winsor Creek, taken February 22, 1954, at Cowles, New Mexico, just above junction with Pecos River. Sent by E. C. Anderson.	9.9 ± 0.2
152	Río Guajataca, Puerto Rico, at Lares, collected March 2, 1954.	0.7 ± 0.2
153	Río Arecibo, Puerto Rico, at Utuado, collected March 2, 1954.	1.1 ± 0.2
155	River Tomokoa, Florida, on Route 92 near Daytona Beach, collected March 19, 1954.	45.4 ± 0.6
156	Alafia River, Florida, on Route 60 about 20 miles east of Tampa, March 22, 1954.	60 ± 3
	E. *Lake Michigan and Other Lakes*	
7	Distilled water from the Jones Chemical Laboratory at the University of Chicago. The intake for the water supply for the southern part of the city is two miles off the shore in southern Lake Michigan. Collected on May 12, 1952.	2.0 ± 0.1
8	Jones Laboratory, Tap water, July 7, 1952.	1.35 ± 0.25
13	Oak Park tap, hot water heater, *ca* 12 years old.	0.62 ± 0.06(1.2)
25	Jones Chemical Laboratory distilled water. Collected on February 6, 1953.	2.4 ± 0.4
32	Jones Laboratory, Tap water, February 13–16, 1953.	1.73 ± 0.06
100	Jones Chemical Laboratory tap water. Collected on October 26, 1953.	1.59 ± 0.10
	Average for Lake Michigan	1.64 ± 0.04
	Calculated average rain from the depth and area of the lake and the mean assay for tritium in the lake:	
143	Lake behind Shasta Dam, California, collected by Dr. L. R. Libby probably January 30 or 31, 1954, certainly not later than February 15, 1954.	2.7 ± 0.15
148	Roundout Reservoir, south shore, collected February 6, 1954, by Seth Harris, Lamont Observatory, 500 yards in front of gate off New York 55. Ice cap over whole reservoir.	7.2 ± 0.3
149	Shandakan Tunnel effluent from Schoharie Reservoir at Allaben, New York, right off route N.Y. 28. Collected February 6, 1954, by Seth Harris.	8.4 ± 0.3
	F. *Hot Springs*	
53	Water from the main reservoir at Hot Springs, Arkansas. Collected on March 18, 1953.	2.5 ± 1.4
93	Water from the Lardarello, Italy, hot springs near Pisa. These hot springs furnish about ⅛ of the electric power in the whole of Italy. The water actually was steam from the volcanic fumaroles.	−0.56 ± 0.538
157	Bowers Hot Springs, Bowers Mansion, Nevada, collected on March 11, 1954.	10.8 ± 11
158	South Steamboat Well, Steamboat Springs, Nevada. Collected March 11, 1954.	6.2 ± 0.4
159	Spring No. 24, Steamboat Springs, Nevada, collected March 11, 1954.	7.1 ± 0.4
160	Spring No. 50, Steamboat Springs, Nevada, collected March 11, 1954.	47 ± 3
161	Wilbur Springs, Colusa County, California, collected probably on March 23, 1954, by Donald E. White, T = 127.2°F. This water is exceptionally high in alkali chlorides, bicarbonates, boron, sulphide, iodine, and other compounds.	1.0 ± 0.1

TABLE 1 (*Continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
162	Devil's Kitchen and Range Spring, The Geysers, collected March 23, 1954, by D. E. White. T = 202°F. No surface discharge, but probably slight sub-surface. Vigorous boiling, evaporation from pool about 15 feet in area. Acid reaction.	10.8 ± 0.4
163	Magnesia Spring, The Geysers, California, collected March 23, 1954, by D. E. White. T = 122°F. Discharge estimated 2 gpm.	11.8 ± 0.6
176	Hot Springs, Arkansas, main reservoir. Collected at Government free Bath House, April 29, 1954.	2.92 ± 0.2
177	Wilson Springs, Arkansas, drill hole No. 1, collected April 29, 1954.	2.06 ± 0.15
185	Morgan Spring, Lassen Park. Growler Spring. This is near neutral alkali chloride-boron-bicarbonate-sulphate spring opposite in type from sample 186. T = 205.4°F; discharge about 8 gpm. Water believed to be in part volcanic but dominantly of surface origin, circulating deeply and mixing. Collected June 8, 1954.	0.57 ± 0.88
186	Sulfur Works, Lassen Park. Big boiling spring. This is an acid spring typical of most of the Lassen hot springs. T = 190°F, no discharge. These springs appear to result from partial condensation of steam that is probably meteoric in origin. Some direct contribution of recently fallen snow. Collected June 5, 1954.	54.2 ± 1.2
	G. *Well Water*	
41	Drill core water from the Wilson uranium prospecting area in Wilson Springs, Arkansas. Taken from the drill core on March 6, 1953.	0.17 ± 0.11
99	Water from the 900 feet deep well at the McDonald Observatory at Fort Davis, Texas. Sample given by Dr. Gerard Kuiper of Yerkes was pumped in June of 1953.	−0.48 ± 0.37 (age greater than 50 years)
89 and 119	Champaign-Urbana city well water. Water taken in July 1953 from well No. 51, located west of Champaign. This well is 296 feet deep and is producing at a rate of 2,225 gallons per minute. The first hundred feet of formation is Wisconsin glacial drift and the next 200 feet are Illinoisan and Kansan drift. The very bottom of the well at 300 feet is at the top of the Pennsylvania system. Nowhere in the entire log of the well is any clay formation which would prevent the downseepage of rain. It was therefore thought that perhaps the well could contain some rainwater. It is generally thought that the well water which supplies the area is ancient and possibly of melted glacier origin. Sample furnished by T. E. Larson, Head, Chemistry Sub-division of State Water Survey.	0.13 ± 0.05 (age greater than 50 years)
	H. *Vintage Wines*	
54	Widmer's New York Riesling wine, Vintage 1952, Naples, New York	5.3 ± 0.3 (5.6 ± 0.3)
55	Widmer's New York Riesling wine, Vintage 1940, Naples, New York	3.2 ± 0.2 (6.6 ± 0.4)
62	Widmer's New York Riesling wine, Vintage 1946, Naples, New York	3.63 ± 0.16 (5.4 ± 0.3)
63	Hermitage Rhône wine, Vintage 1929, Tain, Drôme, France.	1.13 ± 0.38 (4.3 ± 1.4)
64	Hermitage Rhône wine, Vintage 1942. Tain, Drôme, France	2.15 ± 0.21 (3.92 ± 0.4)
65	Hermitage Rhône wine, Vintage 1947, Tain, Drôme, France.	2.15 ± 0.28 (3.0 ± 0.3)
66	Hermitage Rhône wine, Vintage 1951, Tain, Drôme, France.	3.4 ± 0.4 (3.8 ± 0.5)
69	Chateau Laujac Bordeaux wine, Vintage 1928, France.	1.16 ± 0.16 (4.6 ± 0.7)

TABLE 1 (*Concluded*)

Sample no.	Description of Sample	Tritium abundance (T atoms per 10^{18} H atoms)
70	Chateau Laujac Bordeaux wine, Vintage 1934, France.	1.16 ± 0.30 (3.3 ± 0.9)
71	Chateau Laujac Bordeaux wine, Vintage 1939, France.	2.6 ± 0.4 (5.6 ± 0.9)
72	Chateau Laujac Bordeaux wine, Vintage 1945, France.	2.70 ± 0.18 (4.2 ± 0.3)
83	Sherry, Vintage 1942, Jerez de la Frontera, Spain.	1.93 ± 0.27 (3.55 ± 0.5)
84	Sherry, Vintage 1947, Jerez de la Frontera, Spain.	1.99 ± 0.55 (2.67 ± 0.75)
85	Sherry, Vintage 1951, Jerez de la Frontera, Spain.	2.73 ± 1.0 (3.0 ± 1.0)
	K. *Sea Water Samples*	
75	Sea water collected from the beach at Santa Monica, California, on June 8, 1953.	0.54 ± 0.02
115	Sea water collected from the surface of the Gulf Stream on September 11, 1953, at 38° 5′ N, 69° 30′ W. The water temperature was 82°F. This was collected by the ship, Vena, by Mr. Bruce Heezen, Chief Scientist from the Geophysics Section of the Geology Department, Columbia University, the Lamont Laboratory. This is Lamont Sample No. T-32.	0.19 ± 0.05
116	Atlantic sea water taken in Sargasso Sea at 34° 00′ N, 62° 50′ W. Temperature of the water was 81.5°F. Collected following a light drizzle. Lamont Sample No. T-28.	0.29 ± 0.02
117	Atlantic sea water taken from 300 miles from New York on the continental slope at 30° 20′ N and 71° 30′ W. The water temperature was 75°F. Lamont Sample No. T-34.	0.55 ± 0.04
154	Atlantic sea water from the Sargasso Sea at 34° 00′ N. 52° 35′ W. Temperature of the water was 81.5°F. Collected September 7, 1953, immediately following a light drizzle of 1 hour. Lamont Sample No. T-25.	1.6 ± 0.1
	L. *Miscellaneous*	
9	Cistern, Decatur, collected August 6, 1952. Covered loosely about 29 years ago.	5.9 ± 0.5
12	Cistern, Sullivan, Illinois, collected August 6, 1952. Covered with tight iron lid about 14 years ago.	2.9 ± 0.2 (6.3 ± 0.4)
20	Fire extinguisher, Skokie, Illinois. Filled June 5, 1936.	12.5 ± 0.5 (32 ± 1.2)
75	Pacific Ocean, Santa Monica, California. June 8, 1953.	0.54 ± 0.02

IV. DISCUSSION

Recently it has been shown that the tritium produced by the cosmic rays is produced only in part by the neutron reaction mentioned earlier,[5] a large fraction of the tritium being produced by the direct interaction of the primary cosmic rays with the air.[15] It would seem reasonable that whatever the mechanism be by which the cosmic rays produce tritium by bombarding the air, the production rate should vary with latitude in a manner not too dissimilar from that in which the secondary neutrons vary.[16] Simpson has published data for the variation in neutron intensity with latitude at 30,000 feet altitude. Using these data, we can calculate the expected ratio of the worldwide average production rate of tritium, $\overline{Q}$ (T atoms per cm^2 per second) to the local production rate, Q, for various localities. For

[15] FIREMAN, E. L. Phys. Rev. **91**: 922. 1953.

[16] SIMPSON, J. A., JR., Phys. Rev. **83**: 1175. 1951; **84**: 335. 1951.

example, at Lake Mösvan, Norway, the local Q should be multiplied by 0.58 to obtain $\overline{Q}$. At the approximate center of the Mississippi Valley the factor would be 0.64, and at Chicago it would again be 0.58. In this way the data given in Table 1 can be treated and corrected for the expected variation in latitude, though this variation has not yet been completely proved for natural tritium.

The most striking new development in the nature of the results of the assay of natural tritium is included in section K of Table 1, the data on surface sea-water samples. Whereas we had originally supposed that the waves would certainly mix the sea to such an extent that the tritium would be undetectable in surface sea water, we find that indeed this is not so and that surface sea water does contain tritium. Four results given in Table 1, the beach water at Santa Monica (sample 75), the continental shelf Atlantic water (sample 117), the Gulf Stream sample (sample 115), and the Sargasso Sea (sample 116) all strongly indicate that there is definitely measurable tritium in the surface waters. In order to understand this we should know that uniform mixing to a depth of 113 meters would give an average T-value just equal to $\overline{Q}$. This result is obtained if one assumes that all tritium finds its way into the sea eventually before decaying into helium 3—in other words, that the storage in ground water and in the atmosphere is negligible relative to the runoff and direct rain into the oceans. Since, as we will show later, there is little doubt that $\overline{Q}$ is between 0.1 and 0.2 T atoms per cm² per second, one observes that the results in Section K of Table 1 would correspond to a mixing depth of about 100 metres. This comment assumes that the two coastal water samples are high because of rains from the neighboring continents, which are richer, and takes the samples from the Gulf Stream and the Sargasso Sea as being more typical of the open ocean. It seems likely that $\overline{Q}$ is probably less than 0.25, the average of the Gulf Stream and the Sargasso Sea samples, so we may expect that future measurements will show that the sea mixes to a depth of about 50 metres in the lifetime of tritium. This result is in agreement with the notion that some stratification exists in the sea below the surface at a depth of 50 to 100 meters. Measurements of the isotopic oxygen in air dissolved in Pacific Ocean water as a function of depth showed a point of inflection in the isotope ratio at a depth of about 100 meters,[17] and the Baltic is known to behave as almost completely stratified with the bottom of the surface layer lying at about forty meters.[18]

Though further measurements will be required to establish the tritium content of the surface of the ocean, it is clear that this tritium content is low, and water vapor evaporated from the sea is essentially tritium-free. It probably would be well to calculate $\overline{Q}$ assuming sea-water vapor on the average to have about 0.25 T atoms per 10^{18} H atoms. Using this we can set up an equation which expresses the balance between the production and decay processes:

$$\bar{r}_s (\overline{T}_s - 0.25) = 4.7\overline{Q}, \qquad (2)$$

where r_s is the average annual precipitation over the seas in meters, $\overline{T}_s$ is the average tritium content of sea rain in T atoms per 10^{18} H atoms, and $\overline{Q}$ is the cosmic-ray tritium production rate in T atoms per cm² per second. The factor 4.7 is a numerical constant arising from the units. Equation (2) simply assumes that no appreciable storage of tritium in the atmosphere for times comparable to the lifetime of tritium—18 years, average life—occurs, and that essentially all the tritium forms water. The latter assumption is well justified by the measurements of the tritium contents of atmospheric hydrogen that have been made, which indicate well less than 1 percent of the tritium is found in this form. The value of $\bar{r}_s$ used is 0.77 meter per year.[19] Using the data in Table 1 and the latitudinal variation factor described above, we see that $\overline{T}_s$ should lie between 0.9 and 1.0. This gives $\overline{Q}$ values of 0.11 and 0.12, respectively.

This calculation involves the implicit assumption that the tritium made over the

[17] RAKESTRAW, N. M., RUDD, E. P., and Mr. DOLE, Journ. Amer. Chem. Soc. **73**: 2976. 1951.

[18] GUSTAFSON, T. and KULLENBERG, B. Svenska Hydrografisk-Biologiska Kommissionens Skrifter Ny Serie: Hydrografi XIII.

[19] RANKAMA, K. and SAHAMA, Th. G., *Geochemistry*, Chicago, 1950.

oceans is precipitated into the oceans. We know, however, that on the western coasts of the continents considerable tritium from the skies over the seas precipitates on land. Also, our measurements show that rains on the east coast of continents are much higher in tritium. Thus the sea rain just east of the eastern continental coasts must be much richer in tritium than $\overline{T}_s$ as though land-born tritium were precipitating into the sea. In view of the prevailing westerly directions of the winds in the regions measured, these results suggest that $\overline{Q}$ may be somewhat higher than indicated by the ocean data.

We can make similar calculation for the land areas by using the Mississippi Valley average of 6 multiplied by the latitudinal factor 0.6 as a worldwide average for land rain.

It seems that the continental rains must be richer than sea and coastal rains, for two reasons. First, the length of time that the moisture is exposed to contamination by cosmic-ray tritium after leaving the ocean is greater, and secondly, there is less moisture in the air over the continents than over the oceans and coastal regions. This raises the specific activity, that is, the number of tritium atoms per hydrogen atom.

We thus obtain

$$\overline{p}_1(6 \times 0.6 - \overline{T}_s) = 4.7\overline{Q} \qquad (3)$$

where $\overline{p}_1$ is the worldwide average runoff from the land, and the average composition of ocean rain is subtracted to correct for the tritium content of the sea-water vapor coming in over the western coasts and the Gulf of Mexico. The value of $\overline{p}_1$ used is 0.28.[18] The runoff must be used in equation (3) because re-evaporation allows a given tritium atom to be precipitated more than once over land. Only transport into the sea where wave action dilutes the tritium accomplishes the fixation on the surface, and even in this case as we have seen previously the fixation is not complete. The value of $\overline{Q}$ so derived is 0.16. Therefore we conclude $\overline{Q}$ is likely to be close to 0.14, probably to within 20 percent.

Using this result, we calculate the expected tritium contents for average ocean rain and surface-ocean waters on the assumption of uniform mixing to 50 meters. These results are given in Table 2. It is pleasant to observe the agreement with the data given in Table 1.

TABLE 2.—CALCULATED LOCAL TRITIUM PRODUCTION RATES, Q, AND EXPECTED OCEAN RAIN AND SURFACE WATER TRITIUM CONTENTS

Locality	$\overline{Q}/Q$	Q (T atoms/cm²/sec)	$T_{\text{ocean rain}}$ (0.77 metre/year)	$T_{\text{ocean surface}}$ (50 metres mixing)
Chicago	0.58	0.24	2.0	0.55
Norway and the North Atlantic Ocean	0.55	0.26	2.2	0.58
Mississippi Valley	0.60	0.23	1.9	0.53
Honolulu and the Hawaiian Islands	1.90	0.073	0.65	0.17
New Orleans, San Francisco, Southern Italy, Southern Spain	1.00	0.14	1.2	0.32
Puerto Rico	1.25	0.17	0.96	0.26
Marshall Islands	2.40	0.058	0.48	0.13

It is obvious that the data in Table 1 for samples collected later than March 15, 1954, are not germane to our principal point—the cosmic ray tritium. These high numbers were the consequence of the thermonuclear tests in the Pacific in the spring of 1954. Most of our considerations in this paper will ignore them, except in connection with the samples from the hot springs. In this case, the principal question, whether the springs run rain water or not, can be answered nearly as well with the contaminated rain as with the normal rain. In fact, the appearance of unusually radioactive water in the effluent water in several springs must indicate turnover times of a few days or weeks, at most, since the test series began on about March 1. The one rain from Chile collected on April 4, 1954, showed no contamination, while all Northern Hemisphere rain and river waters tested showed it for March 15 onward. Apparently the mixing of water vapor across the equator is much slower than is the east-west mixing.

The large fluctuations in the tritium contents of successive rains in the Chicago area, excluding the large rise in March 1954 due to the test activities in the Pacific, require special consideration in a meteorological

sense. Our basic equations (2) and (3) for the relations between the tritium content, T, and the cosmic-ray production rate, Q, are based on the assumption that tritium cannot stay in the air for years even if it is formed well above the tropopause—the stagnant layer at 30,000 to 50,000 feet between the stratosphere and the troposphere in which the normal weather phenomena occur. Half of the tritium probably is produced on the average above the tropopause. We assume that it cannot stay up there for times comparable to 18 years—the average life of tritium. This assumption does not mean, however, that it may not mix horizontally in an east and west and in a north and south direction rather well due to stratospheric winds before penetrating through the tropopause and being precipitated. Whatever evidence for latitudinal variation of Q is to be found in Tables 1 and 2 should be taken as indicating that the stratospheric storage time is less than the north and south horizontal mixing time.

Assuming perfect vertical mixing, we can speak of the atmospheric moisture content, w, in meters of water per cm^2, and the storage time, τ in years, for the moisture in the air, counting total time elasped in the air after the moisture leaves the ocean and until it returns eventually to the sea as rain or snow or runoff river water. These quantities then will be related to the tritium content of rain, T_r, and the production rate Q, for the open sea by

$$T_r - T_0 = \frac{4.7Q\tau}{w} \qquad (4)$$

where T_0 is the tritium content of ocean-water vapour. For the continental areas this simple equation does not hold, because re-evaporation of precipitated moisture without dilution is an important phenomenon.

The values of w are not well known, but it seems likely from available studies[20, 21] that the range of values will be 0.01 to 0.03, with corresponding average τ values of 0.013 and 0.039 or 4.7 days and 14 days, respectively. At an average wind velocity of ten miles per hour these numbers correspond to transport distances of 1,100 and 3,300 miles respectively.

It is clear that in general land rain should be richer in tritium than sea rain because the atmospheric residence time should be longer and because the mositure content, w, should in general be lower. However, it remains to apply the equation to air masses of known w and with known trajectories so that the variation of Q with latitude can be introduced. It is to be hoped that careful coordination of meteorological data with tritium assays will yield results of importance to meteorology in general.

An attempt has been made to understand the variations of the tritium activity in single rainstorms. Forty samples of individual storms were collected on the campus of the University of Chicago over a period of more than a year. These samples correspond to 16.23 inches of rain, or 46 percent of the total rainfall during this period. The T average of these rains, weighted by the amount of rainfall, gives 8.8 units, which compares reasonably well with the Lake Michigan assay of 7.4. (The Lake Michigan assay of 1.64 is used to calculate the composition of the rain supplying the lake.)

Approximate values for w were computed from radio sounding data for the period of December 2, 1952, to November 20, 1953: monthly means from the Weather Bureau Technical Paper no. 10 had to be employed for the period from November 20, 1953, to March 2, 1954. Values for $w(T - T_0)$ are given in Table 3.

While the measured values for T show a minimum in winter, it can be seen that this effect is over-compensated by multiplication with the amount of precipitable water in the air, thus yielding the total tritium accumulated in the air mass. One then obtains a maximum in summer. This is probably due to the following causes: (1) In summer the wind velocities are lower, therefore the air mass is exposed longer to the tritium production. (2) It is known that the

[20] JACOBS, W. C., *The energy exchange between sea and atmosphere* Bull. Scripps Inst. Oceanogr. 6(2): 22–122. 1951.

[21] BENTON, G. S., ESTOQUE, M. A., and DOMINITZ, J., Johns Hopkins Univ. Department of Civil Engineering Scientific Report no. 1, Contract AF 19(122)-365 of the Geophysics Research Division of Air Force Cambridge Research Center. 1953.

continent is a water donor during the summer-time. This means that the air mass picks up tritiated water from the continent. In winter the large water sources for the atmosphere is the ocean, which is almost dead in tritium.

TABLE 3.—RAINFALL DATA AT THE UNIVERSITY OF CHICAGO CAMPUS

Date	T	$T - T_0$	w in g/cm²	Monthly mean at Joliet, Ill. for w in g/cm²	$w(T - T_0)$
12-2-52	13.2	12.95	1.2	1.0	15.5
1-6-53	7.1	6.85	0.5	0.8	3.4
1-23	9.0	8.75	1.8		15.7
2-11	5.0	4.75	2.0		9.5
2-16	10.8	10.55	0.7	0.85	7.4
2-20	3.3	3.05	2.1		6.4
3-3	9.4	9.15	1.0		9.2
3-7	9.6	9.35	0.8		7.5
3-12	4.75	4.5	2.2	0.98	9.9
3-18	7.9	7.65	2.1		16.1
3-21/22	3.1	2.85	—		—
3-31	9.5	9.25	2.5		23.1
4-3	9.1	8.85	1.8		15.9
4-15	10.0	9.75	1.5	1.48	14.6
4-24	9.0	8.75	4.2		36.7
4-30	6.6	6.35	2.6		16.5
5-22	6.7	6.45	4.8	2.15	30.9
6-5	6.18	5.9	3.25	3.2	19.2
6-25	7.9	7.65	4.1		31.4
7-2	4.3	4.05	4.5		18.2
7-5	7.6	7.35	3.9	3.44	28.6
7-17/20	7.1	6.85	—		—
8-3	3.6	3.35	4.9	3.3	16.4
8-4	17.0	16.75	4.1		68.8
9-4	7.3	7.05	4.3		30.3
				2:5	
9-18	12.0	11.75	3.3		38.8
10-18	9.8	9.55	1.9	1.8	18.2
10-26	19.9	19.65	2.6		51.1
11-20	7.3	7.05	2.8		20.4
11-20	13.5	13.25		1.2	15.9
11-27	34.5	34.25			41.2
12-2/3	7.3	7.05		1.0	7.1
1-20-54	10.5	10.25			8.2
1-21	18.7	18.45		0.8	14.7
1-26	19.4	19.15			15.3
2-5	23.0	22.75			19.3
2-15	9.5	9.25		0.85	7.9
2-16	15.6	15.35			13.0
2-20	4.2	3.95			3.4
3-2	20.8	20.55		0.98	20.1

The argument that the vertical mixing may not be complete would yield a high value in summer also, since thunderstorms in summer are known to reach higher up than snowstorms in winter. But our measurements do not support this thesis, since thunderstorms do not average higher than rains, while snow in general seems to be quite active.

The data given in Table 1, section H, on the tritium contents of vintage wines, together with the comparison of the Lake Michigan average as shown in section E with the general average for the rainfall in the Chicago area, show that without doubt the tritium content of rain up to March 15, 1954, was essentially the same as it had been for the last eighteen years. It is clear, also, of course, that if the calculation can be made for Lake Michigan in which the hydrology is known, and if the checks are satisfactory, that in the case of an unknown lake the measurement of the tritium and a comparison with the rainfall for the general region should give the hydrology, or at least some data on it. For example, the average depth might be calculated, or the average storage time for water in the lake.

The application of natural tritium to the determination of the storage or holdup time for ground waters may be of considerable importance. Some applications have been made and are given in sections F and G of Table 1. In section F data are given for natural hot springs. It seems likely that all of the hot springs utilize surface water except the Lardarello (sample 93) near Pisa, which actually was steam from volcanic fumaroles, the Wilbur Springs at Colusa, Calif. (sample 161), and the Morgan Spring at Lassen Park, Calif. (sample 185).

The wells tested and reported in section G gave old water in agreement with expectations. The lower limit of the age of these waters is 50 years. Thus we cannot distinguish water older than 50 years from very old or juvenile water.

It is clear from an examination of the data in section H of Table 1 that tritium allows one to determine the age of wine. It is also clear that the water in the wines has essentially the same tritium content as the

rain of the general area. For example, the Widmer Winery near Rochester, N. Y., shows a general tritium assay of 5.8 ± 0.3, in good agreement with what one might expect in view of the results for the Mississippi Valley as a whole. The French wines in the Rhône Valley near Bordeaux run around 3½ or 4 of our units; Spanish wines about 3, which within the experimental error agrees with the general rainfall average for the area which is shown by the river-water assay. Therefore it is relatively certain that agricultural products can be dated and also that the presence of rainwater in the agricultural products can be determined. It would be interesting, of course, to test for pumped irrigation water which might possibly be ancient in character, just how effectively the water was incorporated into the crop.

To balance the cosmic-ray production of tritium, there must be some mechanism for the product of the radioactive disintegration of tritium, helium 3, to escape from the earth. Being helium, no chemical compounds can be formed, and being nonradioactive, no nuclear transformations. Therefore, every second for each square centimeter of the earth's surface, 0.14 helium 3 atoms must escape on the average if the cosmic rays have been constant in intensity. A direct analysis of the air shows that there are 1.5×10^{14} helium 3 atoms per cm^2 of the earth's surface. Therefore, we calculate that on the average a helium 3 atom must stay on the earth 34 million years. This escape time may well be about half this, since it is probable that the cosmic rays can also produce helium 3 directly as well as through the tritium, but it seems unlikely that this would do more than double the total rate of production of helium 3. Therefore we rather definitely can say that if the cosmic rays have remained constant for the past 50 or 100 million years, the amount of helium 3 on earth is such as to indicate an escape time of between 20 and 40 million years. This is a rather reasonable magnitude considering the probable escape time for helium 4, as judged from other evidence. One finds in the acceptability of this result some evidence that the cosmic rays indeed have remained constant for this great period of time.

It is by no means obvious that on a time-scale of 18 years the cosmic rays should remain completely constant, if any appreciable portion of them are connected with the solar sunspot cycle of 11 years' duration. The data given in this report so far, however, indicate that there is no real evidence that the present rate of cosmic-ray generation of tritium is any different from what it has been over the past 18 years.

V. ACKNOWLEDGMENTS

The author and his colleagues, Drs. Grosse, Wolfgang, Johnston, Kauffman, vonButtlar, Begeman, and Martel, are all extremely indebted to the Office of Scientific Research of the Air Research and Development Command of the U. S. Air Force for the support of this research. We wish to thank also the many individuals who furnished samples of water and other materials used. We are very grateful to William Timmons for extremely able and devoted operation of the electrolytic plant for concentrating the water samples.

MATHEMATICS.—*Spectroscopic eigenvalue analysis.* C. LANZCOS,[1] Dublin Institute for Advanced Studies, Dublin, Eire. (Communicated by R. K. Cook.)

In honor of Lyman J. Briggs on his eightieth birthday

(Received May 20, 1955)

A method is herein described which transforms the search for the real eigenvalues and eigenvectors of a matrix into the search for hidden periodicities of a function composed of periodic components. The application of the Fourier transform displays the entire eigenvalue spectrum of the matrix in the form of sharp maxima of a Fourier spectrum, in analogy to the operation of a spectroscope. The method is well suited for the big electronic calculators and has the advantage of simple programming, combined with high precision. The same method yields an iterative solution of large-scale linear algebraic systems.

1. *The search for hidden periodicities.* The spectroscope is a physical instrument constructed for the purpose of resolving an arbitrary superposition of periodic functions into its components. Let $f(t)$ be of the following form:

$$f(t) = a_1 \cos \nu_1 t + \cdots + a_n \cos \nu_n t + b_1 \sin \nu_1 t + \cdots + b_n \sin \nu_n t. \tag{1.1}$$

Then the spectroscope transforms this function of t into a new function $F(\nu)$ of the frequency ν, in the following manner. At certain definite values $\nu = \nu_i$ sharp lines appear, the "spectral lines," whose intensity is proportional to $\sqrt{a_i^2 + b_i^2}$. In view of the finite resolving power of the instrument, however, the lines are not sharp but have a finite width. This means that the light intensity is not concentrated at the discrete frequencies $\nu = \nu_i$ but falls off continuously according to the law

$$\frac{\sin (\nu - \nu_i)\, \pi N}{(\nu - \nu_i)\, \pi N}$$

The larger the N, the greater is the resolving power of the spectroscope.

The following method of analyzing the eigenvalues and eigenvectors of a symmetric matrix (or more generally of any matrix whose eigenvalues are all real) is called "spectroscopic" because it imitates mathematically the operation of a spectroscope. The great accuracy of spectroscopic observations is caused by the high resolving power (large N) of spectroscopic instruments. In our operations the value of N will remain within limits which are modest in comparison to the values encountered in physical spectroscopy. And yet the high precision of spectroscopic measurements will be realizable (order of magnitude 10^{-8}), because of the great accuracy with which the basic function $f(t)$ is available.

Let us assume that $f(t)$ is given at the equidistant values of t.

$$t = 0, \tau, 2\tau, \cdots, N\tau. \tag{1.2}$$

We introduce the notation

$$\nu_i \tau = \theta_i \tag{1.3}$$

and restrict all θ_i to the range $[0, \pi]$. Moreover, for our present purposes the sine analysis will not be needed. Hence we assume that the following sequence of ordinates is at our disposal:

$$y_k = a_1 \cos k\theta_1 + a_2 \cos k\theta_2 + \cdots + a_n \cos k\theta_n . \qquad (k = 0, 1, 2, \cdots, N) \tag{1.4}$$

The aim of the spectroscopic analysis (also called "search for hidden periodicities") may be characterized as follows: Given the ordinates $y_k = y_0, y_1, \cdots, y_N$, find the hidden frequencies ν_k (or the θ_k which are proportional to them), and the associated amplitudes a_i.

2. *Solution by Fourier analysis.* The solution of our problem can be given by the method of the Fourier transform (cf. [1], p. 99) suitably modified for the case of discrete data. The process of *integration* has thus to be changed to a process of *summa-*

[1] Former staff mathematician, National Bureau of Standards.

tion. We define the following function of the continuous variable ξ:

$$F(\xi) = \tfrac{1}{2}\, y_0 + y_1 \cos\frac{\pi}{N}\xi + y_2 \cos\frac{\pi}{N}2\xi + \cdots + \tfrac{1}{2}\, y_N \cos\frac{\pi}{N}N\xi. \tag{2.1}$$

This function is periodic with the period $2N$. Moreover, it is an *even* function of ξ:

$$F(-\xi) = F(\xi).$$

Hence it suffices to reduce the range of ξ to $[0, N]$. We will restrict ourselves to *integer values* of ξ: $\xi = k$, which are of particular interest. Hence we will put

$$F(k) = u_k = \tfrac{1}{2}\, y_0 + \sum_{\alpha=1}^{N-1} y_\alpha \cos\alpha\frac{\pi}{N}k + \tfrac{1}{2}\, y_N \cos N\frac{\pi}{N}k. \tag{2.2}$$

These u_k can be plotted as isolated amplitudes at the equidistant abscissas $k = 0, 1, 2, \cdots, N$. The sharp maxima of these amplitudes[2] will reveal the frequencies which are present in the original function $f(t)$ and the strength with which they are represented.

We shall first write down the Fourier transform $F(\xi)$ of the specific function $y_k = a_i \cos k\theta_i$. However, for the purposes of mathematical operations it will be convenient to replace the frequencies θ_i by proportional quantities, to be denoted by p_i:

$$\theta_i = p_i \frac{\pi}{N}. \tag{2.3}$$

Let us introduce the following function of x:

$$\phi(x) = \tfrac{1}{4} \sin \pi x \cot\frac{\pi x}{2N}. \tag{2.4}$$

Then we obtain

$$F(\xi) = \phi(p - \xi) + \phi(p + \xi). \tag{2.5}$$

[2] For the sake of distinction we will refer to the y_k (equidistant ordinates of the given function $f(t)$) as the "ordinates," and the u_k (equidistant ordinates of the Fourier transform) as the "amplitudes."

For all practical purposes the function (2.4) can be replaced by the simpler function

$$\phi(x) = \frac{N}{2}\frac{\sin \pi x}{\pi x} \tag{2.6}$$

An ideal situation exists when all the p_i of a given problem are *integers*. Then

$$\theta_i = m_i \frac{\pi}{N}, \tag{2.7}$$

where m_i is an integer between 0 and N. The Fourier transform u_k of the function

$$y_\alpha = a_i \cos m_i \frac{\pi}{N}\alpha \tag{2.8}$$

is now reduced to a *single line* at the point $k = m_i$, with the amplitude $\frac{N}{2}a_i$. The distribution of the u_k consists now of isolated lines. The position and magnitude of these lines determine directly the θ_i and the a_i.

In the general case we can put

$$p = m + \epsilon, \tag{2.9}$$

where m is an integer and ϵ a quantity between 0 and 1. In this case we no longer obtain a single line for the Fourier transform of a cosine function, but a group of lines clustered around the maximum at $k = m$, with slowly decreasing amplitudes. We will write

$$k = m + \mu \tag{2.10}$$

(μ = integer) and obtain as the transform of the function $\cos \theta\alpha$ the amplitudes

$$u_{m+\mu} = \frac{N}{2}\frac{\sin \epsilon\pi}{\pi}\frac{(-1)^\mu}{\epsilon - \mu} \tag{2.11}$$

The sharp peak at $\mu = 0$ is still there but the neighboring amplitudes are no longer zero. They fall off rather slowly (if ϵ is near to $\frac{1}{2}$), with alternating signs, and influence the position of other maxima, if these maxima are not separated by large distances, i.e., if N is not excessively large.

We can greatly reduce the mutual interference of neighboring peaks if instead of operating with the amplitudes themselves we

investigate each combination of three neighboring amplitudes. The second difference of the function $1/(\epsilon - x)$ falls off with the *third power* of $\epsilon - x$ and hence becomes quickly negligible. In view of the factor $(-1)^\mu$ in (2.11), the second difference has to be replaced by the second *sum*:

$$v_k = u_{k-1} + 2u_k + u_{k+1}. \tag{2.12}$$

The sign of the u_k generally alternates between + and −, but this regular ± pattern is occasionally disturbed by a + +, or − − sequence. This irregularity reveals the nearness of a peak, regardless of the magnitude of the u_k. We underline each + + or − − pair and draw all further conclusions from them and their neighbors. The order m of the amplitude u_m, belonging to the first member of the pair, constitutes the integer part of p. The fractional part ϵ is now determined as follows. We can put

$$u_{m+\mu} = \frac{(-1)^\mu}{\epsilon - \mu} \tag{2.13}$$

Then

$$v_m = \beta\left(\frac{2}{\epsilon} - \frac{1}{\epsilon - 1} - \frac{1}{\epsilon + 1}\right)$$

$$= \frac{2\beta}{\epsilon(1 - \epsilon^2)}, \tag{2.14}$$

$$v_{m+1} = \frac{2\beta}{\epsilon(1 - \epsilon)(2 - \epsilon)}.$$

We now form the ratio

$$q = \frac{v_m}{v_{m+1}} = \frac{2 - \epsilon}{1 + \epsilon}, \tag{2.15}$$

whence

$$\epsilon = \frac{2 - q}{1 + q}. \tag{2.16}$$

The strength β of the peak is evaluated as follows:

$$\beta = \epsilon(1 - \epsilon)(u_m + u_{m+1}). \tag{2.17}$$

Finally, going back to the original frequency and amplitude of the cosine component of the function (1.1), we get

$$a_i = \frac{2}{N}\frac{\pi}{\sin \pi\epsilon}\beta \tag{2.18}$$

and

$$\theta_i = (m + \epsilon)\frac{\pi}{N}. \tag{2.19}$$

This method of resolving a function, given in equidistant ordinates, into its periodic components is more accurate than the customary numerical schemes pursued in the "search for hidden periodicities" (cf. [9], p. 349). It is shaped to the demands of a problem in which the basic ordinates y_n are given with *high accuracy*; we need not rely on the assumption that the frequencies which are present in $f(t)$ are necessarily widely separated. If N is sufficiently large (order of magnitude 1,000) and the functional ordinates given with an accuracy of 10^{-6}, we can obtain an accuracy of 10^{-6} or higher, for the determination of the θ_i.

3. *The Chebyshev polynomials.* Let x be an ordinary algebraic quantity, limited to a real positive range between 0 and 1. We generate a succession of polynomials by the following recurrence relations (cf. [10], p. XI):

$$\begin{aligned} b_0 &= 1, \quad b_1 = 1 - 2x \\ b_2 &= 2(1 - 2x)b_1 - b_0 \\ b_3 &= 2(1 - 2x)b_2 - b_1 \\ &\cdots \\ b_N &= 2(1 - 2x)b_{N-1} - b_{N-2} \end{aligned} \tag{3.1}$$

The quantities thus generated have the following significance:

$$b_k = \cos k\theta, \tag{3.2}$$

where

$$\sin^2\frac{\theta}{2} = x. \tag{3.3}$$

We now replace x by the matrix A. If we assume that the eigenvalues of A are all real, positive, and limited to the range [0, 1], we may construct the "operating matrix"

$$C = 2I - 4A \tag{3.4}$$

and generate a succession of vectors by the following iteration scheme; where b_0 is an arbitrary trial vector:

$$\begin{aligned} b_1 &= \tfrac{1}{2}Cb_0 \\ b_2 &= Cb_1 - b_0 \\ b_3 &= Cb_2 - b_1 \\ &\cdot \\ &\cdot \\ &\cdot \\ b_N &= Cb_{N-1} - b_{N-2}\,. \end{aligned} \tag{3.5}$$

Let us analyze b_0 in the reference system of the principal axes of A. We will call these principal axes $w_1, w_2, \cdots, w_n$;

$$b_0 = \beta_1 w_1 + \beta_2 w_2 + \cdots + \beta_n w_n\,. \tag{3.6}$$

Then

$$\begin{aligned} b_k = {} & (\beta_1 \cos k\theta_1)w_1 + (\beta_2 \cos k\theta_2)w_2 \\ & + \cdots + (\beta_n \cos k\theta_n)w_n \end{aligned} \tag{3.7}$$

where the θ_i are in the following relation to the eigenvalues λ_i of the matrix A:

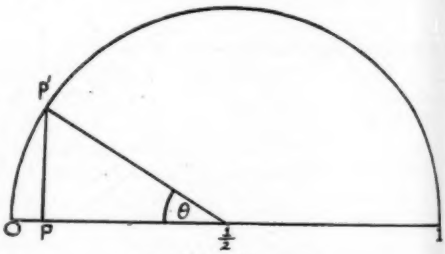
$$\lambda_i = \sin^2 \frac{\theta_i}{2} = \frac{1 - \cos \theta_i}{2} \tag{3.8}$$

We will now pick out one definite component b_k—e.g., the first component of each successive vector b_k—and consider this one-dimensional sequence of quantities as the y_k-sequence (1.4):

$$y_k = b_0^{(i)},\ b_1^{(i)},\ b_2^{(i)},\ \cdots,\ b_N^{(i)} \tag{3.9}$$

We subject this sequence to a Fourier analysis, obtaining the amplitudes (2.2). The isolated maxima of this sequence, evaluated according to sec. 2, will determine all the θ_i—and thus also all the λ_i—with high precision.

4. *Programming for the large electronic calculators.* In contrast to the author's earlier method of "minimized iterations" (cf. [4]; see also [2] and [8]), the present method is far less economical in the number of iterations employed. The total number of iterations N must exceed the order n of the matrix by a factor of 10 to 20, in order to guarantee the proper independence (and thus easy separability) of the peaks. On the other hand, the present method recommends itself by the simplicity of the operations and the ease of its programming for the electronic computer. Since the successive iterations follow each other quite automatically without any disturbance, the generation of the b_k vectors is a quick process, even in the case of large matrices. Moreover, in the previous method the eigenvalues λ_i did not appear explicitly but had to be obtained as the roots of an algebraic equation. In the present procedure, the eigenvalues come directly in evidence by the position of the maxima of a set of Fourier amplitudes. Furthermore, the usual difficulty of properly protecting the small eigenvalues against the encroachment on the part of the large eigenvalues is here completely circumvented by the method of projecting them on a semicircle with the radius $\frac{1}{2}$. On the circle the question of magnitude loses its meaning, and all eigenvalues come into play on an equal footing. In this manner, a single Fourier analysis is able to display the *entire* spectrum of a matrix.



$\lambda = \frac{1}{2} - \frac{1}{2}\cos\theta$

The procedure consists of two phases:

1. The generation of the vectors b_k.

2. The Fourier analysis of these vectors.

The latter analysis need not be carried out with the entire vector but only with *a single component* of each of these vectors. In actual practice, it is advisable to isolate *two* sets of components. We can use the second set for checking purposes and also for the testing of multiple eigenvalues, as we will see later, in sec. 9.

The symmetry of the matrix A is not required. It suffices to know that all the eigenvalues of A are real.[3] However, the

[3] The case of complex eigenvalue will be treated in a subsequent paper.

symmetry of A has an important advantage. If A is symmetric, then the eigenvectors w_i are orthogonal to each other. Since we defined the vectors b_k by a process which never multiplies the eigenvectors by anything larger than 1, we know in advance that the absolute value of the vectors b_k (in the case of a symmetric matrix) can never grow beyond that of the first vector b_0. Hence we need not program for overflow. If the capacity of the machine is, let us say, 10 decimal digits, we can fill up the cells connected with b_0 with 9 decimal random numbers. Since the magnification factor in any component cannot go beyond the factor $\sqrt{n}$, the provision of one empty digit in front of the number suffices to take care of the overflow, no matter how far we extend the procedure.

5. *Generation of the vectors* b_k. If the original matrix A is an arbitrary matrix, except for the fact that the reality of the eigenvalues is known in advance, we can estimate the absolutely largest eigenvalue by Gersgorin's method. Taking the sum of the absolute values of each row (or column) and choosing the largest of these n positive numbers, we obtain an upper bound, s, on the eigenvalues of A. If we now put

$$C = \frac{2}{s} A \tag{5.1}$$

we can be sure that the eigenvalues of this matrix will be limited by -2, $+2$.

If, moreover, we know in advance that all the eigenvalues of A are positive, we put

$$C = 2I - \frac{4}{s} A. \tag{5.2}$$

Gersgorin's method generally overestimates the largest eigenvalue of A. This has the disadvantage that the λ-spectrum will be squeezed into a too small portion of the semicircle, leaving the remaining part unused. It is advisable therefore to go through a preliminary Fourier analysis for a closer evaluation of the smallest and the largest eigenvalue of A, but with no demands of precision. For this purpose a relatively small value of N, e.g. 40, is sufficient, since we do not mind if the λ-spectrum is crowded. We are interested only in the lower and the upper limits λ_b and λ_s (in rough approximation). Then we put

$$C = 2\frac{\lambda_s + \lambda_b}{\lambda_s - \lambda_b} I - \frac{4}{\lambda_s - \lambda_b} A \tag{5.3}$$

and thus ascertain that the eigenvalues will spread over the entire semicircle.

The generation of the vectors b_k occurs with the help of the simple iteration scheme (3.5).

6. *Fourier analysis of the* b_k. We isolate one component (or possibly two components) of each vector and subject this one-dimensional sequence of numbers y_k to a Fourier analysis. The very first and the very last element, i.e. the components belonging to b_0 and b_N, are immediately divided by 2. In our subsequent formulae we will assume that y_0 and y_N refer to the halved ordinates. The Fourier analysis consists in multiplying the given sequence y_k by the coefficients of a preassigned matrix Γ, defined by

$$\gamma_{ik} = \cos ik\frac{\pi}{N} \tag{6.1}$$

$$u_k = \sum_{\alpha=0}^{N} \gamma_{k\alpha}\, y_\alpha \tag{6.2}$$

We can generate the coefficients γ_α of y_α concurrently with the summation, on the basis of the following recurrence scheme:

$$\begin{aligned} \gamma_0 &= 1 \\ \gamma_1 &= \rho_k, \\ \gamma_2 &= 2\rho_k\gamma_1 - \gamma_0 \\ \gamma_3 &= 2\rho_k\gamma_2 - \gamma_1 \\ &\cdots \\ \gamma_N &= 2\rho_k\gamma_{N-1} - \gamma_{N-2} \end{aligned} \tag{6.3}$$

where the keyvalues $\rho_k = \cos k\frac{\pi}{N}$ can be taken from a trigonometric table. But it is still simpler to let the machine evaluate and store the ρ_k, by taking only the single value $\rho_1 = \cos\frac{\pi}{N}$ from the trigonometric table and then generate the remaining ρ_k on the basis of the recurrence relation (6.3).

We have now obtained the amplitudes

$$u_0 , u_1 , u_2 , \cdots , u_N \tag{6.4}$$

which will now be examined for peaks, following the procedure of sec. 2. The presence of a peak is demonstrated by a $+\ +$, or $-\ -$ sequence which interrupts the regular $\pm$ sequences. Such pairs are underlined and the calculation of the eigenvalues is based on these pairs, augmented by one neighbor to the left and to the right:

$$u_{m-1} , \underline{u_m} , \underline{u_{m+1}} , u_{m+2} . \tag{6.5}$$

We form the ratio

$$q = \frac{u_{m-1} + 2u_m + u_{m+1}}{u_m + 2u_{m+1} + u_{m+2}} \tag{6.6}$$

and

$$\epsilon = \frac{2 - q}{1 + q} \tag{6.7}$$

Then

$$\lambda' = \frac{1 - \cos (m + \epsilon) \frac{\pi}{N}}{2} \tag{6.8}$$

The corresponding eigenvalue of the original matrix A finally becomes

$$\lambda = \lambda_b + (\lambda_{b'} - \lambda_b)\lambda' \tag{6.9}$$

Since the customary trigonometric tables divide the semicircle into 180°, it is convenient to choose for N, the total number of iterations, some multiple of 180. If for example $N = 180$, the angle θ_i, determined by the integer m_i plus the correction ϵ_i, is directly given in degrees. If $N = 1800$, the circle becomes divided into tenths of degrees (i.e. 6′), and $\frac{m_i + \epsilon_i}{10}$ gives θ_i directly in degrees.

7. *The problem of noise.* We would assume that an iterative scheme, if pushed too far, might lead to a dangerous accumulation of rounding errors. In actual fact the generation of the vectors b_k seems to be remarkably free of rounding errors. The rounding errors accumulate rather slowly and in the same ratio as the peaks increase in size. Hence the "signal to noise ratio" does not deteriorate with increasing N. Many hundreds, and even thousands of iterations can be performed without affecting the precision with which the θ_i are obtainable. The detection of certain very small eigenvalues demands occasionally a very large number of iterations. Our experience seems to indicate that the rounding errors have no vitiating influence on the result, even under such unfavorable conditions.

The problem of noise can best be studied with the help of a matrix C which is so constructed that all its eigenvalues are of the form

$$\lambda_i = 2 \cos m_i \frac{\pi}{N} \tag{7.1}$$

where m_i is an integer between 0 and N (cf. (2.8)). In this case the field of the u_k should consist of n isolated amplitudes only, separated by completely blank spaces. Anything found in the blank spaces is due to noise. Experiments with matrices of low order have shown that even after hundreds of iterations the blank spaces remained blank with an accuracy of 10^{-8}. Experiments with large matrices and thousands of iterations are not yet available.

8. *Eigenvectors.* The effect of the Fourier analysis is that of isolating one particular periodic component out of a mixture of periodic components. This is precisely our aim when attempting to obtain the eigenvectors w_i of the matrix A. As the equation (3.7) shows, the vector b_k is a superposition of periodic components with amplitudes which are proportional to w_i. This makes it possible to extend the technique of the Fourier analysis from the determination of the *eigenvalues* to the determination of the *eigenvectors*. Let a peak be near to a certain $k = m$. Then the operation

$$\begin{aligned} u_m = {} & \tfrac{1}{2} b_0 + \left(\cos m \frac{\pi}{N}\right) b_1 \\ & + \left(\cos 2m \frac{\pi}{N}\right) b_2 + \cdots \\ & + \tfrac{1}{2} \left(\cos Nm \frac{\pi}{N}\right) b_N \end{aligned} \tag{8.1}$$

will generate a vector which strongly emphasizes the eigenvector w_i. We may thus apply the process of (6.2), now extended over the *entire vector* and not merely over one element of the vector. The vectors b_k must be preserved in their entirety for this computation. In contrast to the previous Fourier analysis, which demanded a systematic scanning for all values of k between 0 and N, the present process has to be carried out only for those specific m-values which belong to the eigenvalues.

Again the purification can be enhanced if we operate with second differences which in actual fact become second *sums*. In addition to the u_m-value which is nearest to a peak, we also evaluate the u_k for the left and right neighbors $k = m - 1$ and $k = m + 1$ and then take the combination

$$v_m = u_{m-1} + 2u_m + u_{m+1} \tag{8.2}$$

This vector will be proportional to w_i with smaller contamination on the part of the other w_k than if u_m alone were taken.

9. *Multiple eigenvalues.* If we count the number of maxima of the Fourier analysis and find that their total number adds up to the order of the matrix, we may conclude that *all* the eigenvalues of our problem have become evident. If the total number is less than n, then a further investigation is needed concerning the missing eigenvalues. One possible reason for the lacunae is that the trial vector b_0 possesses accidental "blind spots" in the direction of some of the eigenvectors. This possibility is considerably diminished by the fact that the components of b_0 were chosen as 9-digit random numbers. At all events, if we have isolated a second set of b_k components, it is advisable to repeat the Fourier analysis for this set and see whether more peaks can be recorded in the second analysis.

If this is not the case, the question of the missing eigenvalues can be further clarified by repeating the entire procedure with a new random vector b_0'. If this analysis reveals new peaks, this demonstrates that our original trial vector had accidental degeneracies which were removed in the new analysis. But if the deficiencies still exist, we may assume that some of the eigenvalues are multiple eigenvalues or eigenvalues which fall too close together.

In this case it becomes imperative to find out which of the eigenvalues can be trusted to be single and which cannot. The decision can be made by the following procedure. We assume that we possess the Fourier analysis of *two* elements of the original trial vector, and the same analysis of the corresponding elements of the new trial vector. We form the second sum in the neighborhood of a peak, for both elements in the original set and compute the ratio

$$r = \frac{u_{m-1}^{(1)} + 2u_m^{(1)} + u_{m+1}^{(1)}}{u_{m-1}^{(2)} + 2u_m^{(2)} + u_{m+1}^{(2)}} \tag{9.1}$$

Now we do the same for the new trial vector. If r turns out to be the same in both cases, we have demonstrated that the eigenvalue in question is *single*. If the two ratios are not the same, we have demonstrated that the eigenvalue in question represents two (or more) collapsing eigenvalues, or at least two (or possibly more) maxima which are very nearly the same and which have to be separated by further efforts.

10. *Separation of two very close eigenvalues.* The separation of several excessively close eigenvalues is not an easy problem since two such eigenvalues operate also physically together and exceedingly refined observations ("fine structure analysis") are demanded for their separation. However, *two* very close eigenvalues can still be separated with relatively simple tools. We start with u_m and u_{m+1} knowing that a maximum exists between them. However, we have good reasons to suspect that not one but two peaks can be found between these two amplitudes. We will now operate with *five* successive amplitudes, viz.

$$u_{m-2}\,,\ u_{m-1}\,,\ \underline{u_m}\,,\ \underline{u_{m+1}}\,,\ u_{m+2} \tag{10.1}$$

and assume that *two* eigenvalues exist in this region. Hence we now have two p-values, namely $p_1 = m + \epsilon_1$ and $p = m + \epsilon_2$. We introduce

$$\begin{aligned} \epsilon_1\epsilon_2 &= \rho \\ \epsilon_1 + \epsilon_2 &= \sigma \end{aligned} \tag{10.2}$$

and obtain two linear equations for the determination of ρ and σ. These two equations are as follows:

$$\begin{aligned}&(u_{m-2} + 3u_{m-1} + 3u_m + u_{m+1})\\&\quad + (2u_{m-2} + 3u_{m-1} - u_{m+1})\\&\quad + (4u_{m-2} + 3u_{m-1} + u_{m+1}) = 0\\&(u_{m+2} + 3u_{m+1} + 3u_m + u_{m-1})\\&\quad - (2u_{m+2} + 3u_{m+1} - u_{m-1})\\&\quad + (4u_{m+2} + 3u_{m+1} + u_{m-1}) = 0.\end{aligned} \tag{10.3}$$

We solve these two equations for ρ and σ and then find the roots of the quadratic equation

$$x^2 - \sigma x + \rho = 0 \tag{10.4}$$

which gives us ϵ_1 and ϵ_2.

If the determinant of this linear set becomes too small, this is an indication that the two peaks are too close together to be numerically separable (except by an increase of N). In that case the two equations collapse into one but this one equation suffices for the localization of the double-peak since now we can put $\rho = 0$, $\sigma = \epsilon_1$.

This separation technique could be extended to more than just two nearly equal peaks. The difficulty is, however, that the calculations become very sensitive to the contaminating influence on the part of the external peaks. For this reason we should first obtain the critical eigenvector by the v_m-method described in sec. 8. This vector is now a linear superposition of the two or more eigenvectors which belong to the closely bunched eigenvalues, without being contaminated by the external eigenvectors. If we use this vector as the trial vector b_0 of the recurrence scheme (3.5), the subsequent Fourier analysis has a better chance of separating the closely spaced eigenvalues since the interference from the external peaks is removed.

11. *Very small eigenvalues.* In the case of positive definite matrices we are sometimes interested in the determination of a few excessively small eigenvalues. For very small eigenvalues of A (largest eigenvalue not exceeding 1) the relation (3.8) becomes

$$\lambda_i = \left(\frac{p_i \pi}{2N}\right)^2 \tag{11.1}$$

The appearance of N^2 in the denominator makes even very small eigenvalues detectable. However, the case of very small eigenvalues requires special attention, because of the following circumstance. The amplitudes u_k belong to a circle and do not terminate at either end. The full period includes $2N$ terms. Every peak on the positive side has an accompanying peak on the negative side, due to the relation

$$u_{-k} = u_k \tag{11.2}$$

The very small eigenvalues are thus disturbed by the presence of a near peak on the negative side. Beyond $k = 5$ the influence from the negative side becomes negligible but this is not the case in the realm of the smallest eigenvalues. In this realm a special numerical scheme comes into operation.

It is of advantage to avoid eigenvalues in the range between $k = 0$ and $k = 2$ altogether since in this range it is difficult to keep down the interference from the larger eigenvalues. We can push out the spectrum of the matrix A by putting a properly chosen constant in the main diagonal. We assume that the eigenvalues of A are already normalized to the range [0, 1]. We now modify A to

$$A' = A + \left(\frac{\pi}{N}\right)^2 I \tag{11.3}$$

This means that the matrix C will be defined by

$$C = \left[2 - 4\left(\frac{\pi}{N}\right)^2\right] I - 4A \tag{11.4}$$

The effect of this modification is that the eigenvalues of the new problem become

$$\lambda' = \lambda + \left(\frac{\pi}{N}\right)^2 \tag{11.5}$$

This means—since A has no negative eigenvalues—that the eigenvalues of the modified matrix cannot start below $p = 2$. After obtaining the eigenvalues of the new matrix, we finally return to the original matrix by

subtracting from all λ_i' the same constant $\left(\frac{\pi}{N}\right)^2$.

We will now assume that the range between $p = 2$ and $p = 4$ may contain *two* eigenvalues. The separation of these close eigenvalues occurs again in analogy to the procedure of sec. 10. Once more we introduce the sum and the product of the ϵ-values, but with the following modification. They now appear in *squared* form:

$$\epsilon_1^2\epsilon_2^2 = \rho \qquad \epsilon_1^2 + \epsilon_2^2 = \sigma \tag{11.6}$$

Moreover, ϵ_1 and ϵ_2 are not restricted to the range [0, 1] because the roots are measured *from zero* and we obtain for the associated eigenvalues directly

$$\lambda_1' = \frac{\epsilon_1^2}{4}\left(\frac{\pi}{N}\right)^2 \qquad \lambda_2' = \frac{\epsilon_2^2}{4}\left(\frac{\pi}{N}\right)^2 \tag{11.7}$$

The two linear equations which determine σ and ρ have coefficients which are linear conbinations of the first five u_k-values: $u_0, u_1, \cdots, u_4$. The coefficients of the first equation are displayed in the following scheme:

(11.8)

	ρ	$-\sigma$	1	
u_0	10			
u_1	15	15	15	
u_2	6	24	96	$= 0$
u_3	1	9	81	
u_4				

(This means that the factor of ρ is for example

$$10u_0 + 15u_1 + 6u_2 + u_3$$

and so on.) The coefficients of the second equation become similarly:

	ρ	$-\sigma$	1	
u_0	-105			
u_1	0			
u_2	252	1008	4032	$= 0$
u_3	192	1728	15552	
u_4	45	720	11520	

If the two linear equations are not solvable due to the smallness of the determinant, we obtain only *one* eigenvalue but again we can put $\rho = 0$, $\sigma = \epsilon_1^2$, and the second equation can be discarded. Beyond $k = 4$ the determination of ϵ by the ratio of two second sums (cf. sec. 2) and the separation of two close eigenvalues according to sec. 10 becomes applicable again.

12. *Acknowledgments.* The "spectroscopic eigenvalue analysis" was developed in the winter 1953–54, during the author's stay with North American Aviation, Los Angeles, Calif. The splendid support he received in his lecturing and research activities during this time will remain indelible in his memory. The almost daily discussion with Charles Davis and his staff was a constant source of inspiration. The access to the "701," the electronic calculator of the I.B.M. Company, made it possible to test the practical feasibility of the methods. The programming and coding for the 701 were planned and carried out by Owen Mock with great ingenuity. Although only matrices of low order (6 to 8) were employed, the generation of the b_k vectors and the subsequent Fourier analysis could be studied in detail. Runs first of 180, then of 720, and finally of 1280, iterations were generated, and the non-accumulation of noise was demonstrated. Results were checked by applying another precision method for finding the eigenvalues of a matrix.

Experiences with large-scale matrices and a statistical investigation of the noise problem and its relation to the position of the Fourier peaks are not yet available.

REFERENCES

[1] COURANT, R., and HILBERT, D. *Methods of mathematical physics* **1.** New York, 1953.
[2] HESTENES, M. R., and STIEFEL, E. Nat. Bur. Standards Journ. Res. **49:** 409. 1952.
[3] JAHNKE, E., and EMDE, F. *Tables of functions with formulae and curves.* New York.
[4] LANCZOS, C. Nat. Bur. Standards Journ. Res. **45:** 255. 1950.
[5] LANCZOS, C. Nat. Bur. Standards Journ. Res. **49:** 33. 1952.
[6] LANCZOS, C. Proc. Assoc. Computing Mach.: 124. 1953.
[7] MILNE, W. E. *Numerical calculus.* Princeton, 1949.
[8] STIEFEL, E. Zeits. Ang. Math. Phys. **3:** 1. 1952.
[9] WHITTAKER, E. T., and ROBINSON, G. *Calculus of observations.* London, 1924.
[10] Tables of Chebyshev Polynomials, NBS Applied Math. Series No. 9. 1952.

BOTANY.—*A 2–4–2 chimera of McIntosh apple.* HAIG DERMEN, Horticultural Crops Research Branch, U. S. Department of Agriculture.

(Received August 3, 1955)

In 1948, a large-fruited sport of var. 'McIntosh' apple, now known as 'Kimball Giant McIntosh', was reported as being a 2–4–4 chimera (Dermen and Darrow, 1948). This particular chimeral makeup was determined by examination of a shoot tip of one of six one-year-old plants propagated from the sport portion of the mother tree. Two of the five remaining trees were potted and disbudded to induce endogenous (adventitious[1]) shoot development (for the method to induce endogenous shoots in the apple see Dermen, 1948). Along with the tree that was examined cytologically, they were left in the greenhouse until fall when they were planted in the orchard. The other three trees were planted in the orchard when they were received. One of these was left intact but two were disbudded and died subsequently. The present report is based principally on the cytohistological study of the tree planted intact in the orchard. Some portions of this report, including illustrations of material in Fig. 1 have appeared previously (Dermen, 1951a, b). They are given here to elucidate certain points in this report and to help to enable the reader to follow some pertinent discussions.

On one of the two greenhouse disbudded trees, a single endogenous bud developed and a cluster of shoots grew from it. On cytohistological examination, the shoots were found to be homogeneously *diploid* instead of tetraploid as expected (Dermen, 1951a). On the other disbudded tree, four endogenous buds (*a*, *b*, *c*, *d*) developed (Fig. 1-A). Buds *a*, *b*, and *c* were along a vertical line on the stem, whereas bud *d* was located at a point off the line from the other buds. Subsequently shoots developed from buds *a* and *d* only (Fig. 1-B).

A cluster of shoots from bud *a* was found to be diploid like the cluster of shoots from the first disbudded tree. The shoot from bud *d*, however, was *homogeneously tetraploid*. These findings suggested that the young trees from which the endogenous shoots were obtained were chimerically either 2–4–2 or a modification of it (Dermen, 1951a, b). They could not have been 2–4–4 chimeras since only homogeneously tetraploid shoots can develop endogenously from this type (Dermen, 1955).

Cytohistological examination of a number of shoot tips from the tree grown intact in the orchard revealed the true condition. Some of these were found to have the 2–4–4 constitution, like that previously reported (Dermen and Darrow, 1948); but others were found to be of a 2-4-2 chimeral type. A shoot tip of one twig with the latter constitution is illustrated in Fig. 2-A, a longisection through the center of the growing point. Layers of cells in the growing point are marked L-I (first layer), L-II (second layer) and L-III (third layer). In this material, L-II appears as a wide band because of its being composed of larger cells as compared with the adjacent narrow layers with smaller cells. Nuclei in cells of L-II were definitely larger than those in cells of other layers. This was determined by the study of sections under high magnification. It has been demonstrated on several occasions (Dermen, 1947, 1951b, 1953) that large nuclei in such meristematic tissues are associated with tetraploidy. Nevertheless adequate cytological examinations were made and the exact ploid nature of each apical layer and tissues derived from them was determined.

In Fig. 2-B, a transverse section of the stem about four millimeters back of the tip shown in Fig. 2-A, a solid ink line was drawn to indicate the boundary line between tetraploid and diploid regions in the cortical tissue (for method of determination of the boundary line see Dermen, 1947, 1951b, 1953). The tetraploid part of the cortex in this material extended from the epidermis to the solid ink line. The epidermis and the tissue inside the solid line were diploid. The

[1] For the use of the term *endogenous* in place of or along with adventitious, see the article by the author (Dermen, 1955).

FIG. 1.—A, A disbudded one-year-old tree propagated from the large-fruited sport of a McIntosh apple tree, with four endogenous buds, *a*, *b*, *c*, and *d*; natural size. B, The same tree as in Fig. 1-A photographed a month later. A cluster of shoots developed from bud *a*, none from *b* and *c*, and one from bud *d*; shoots from *a* were diploid and the one shoot from *d* was tetraploid. ×½.

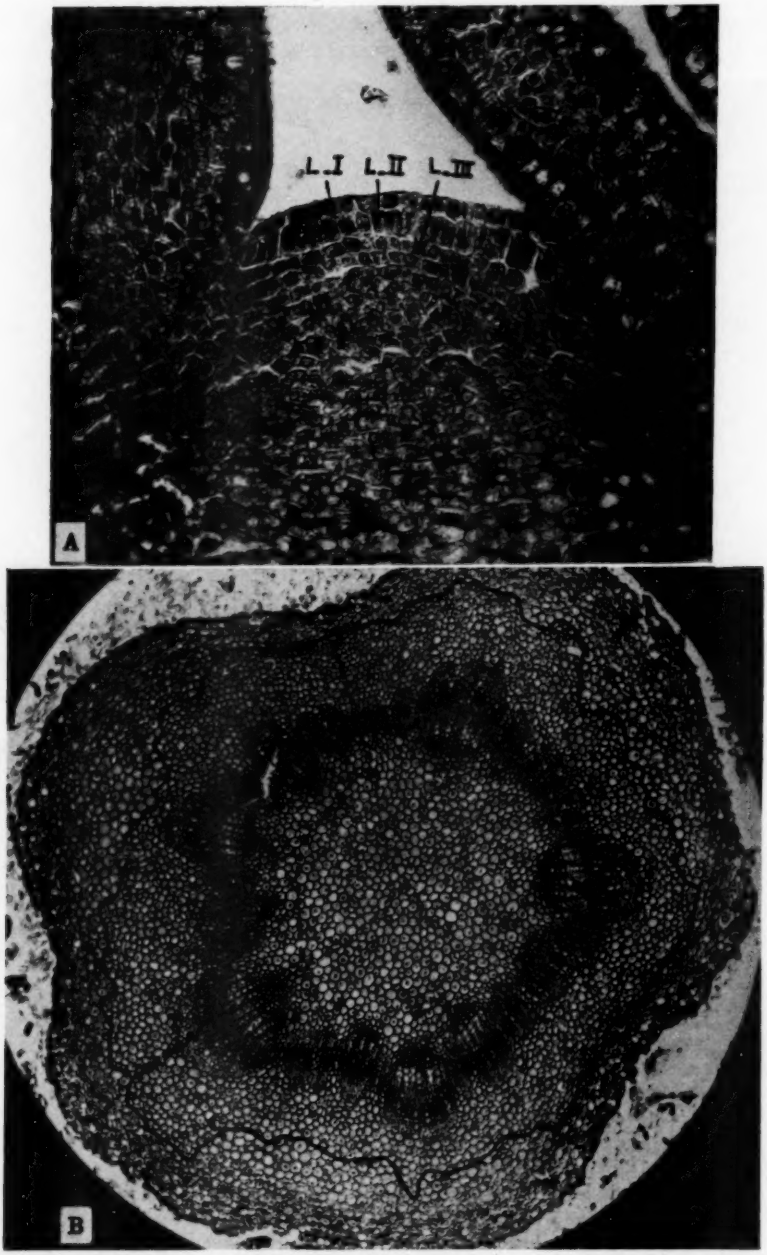


FIG. 2.—A, Longisection of a shoot tip from a tree also from the McIntosh sport; L-II was tetraploid and L-I and L-III were diploid. ×400. B, Transection of stem back of the tip shown in Fig. 2-A. Details are given in the text. ×130.

significance of the dotted line in this figure is pointed out in the discussion.

DISCUSSION

The chimeral nature of the Kimball Giant McIntosh sport was first reported to be the 2–4–4 type (Dermen and Darrow, 1948). However, the development of both diploid and tetraploid shoots from a disbudded tree propagated from the sport tree suggested that its constitution must have been 2–4–2 and that the 2–4–4 chimera represented a form derived from the 2–4–2 chimeral condition (Dermen, 1951a and b).

It has been pointed out that endogenous buds on the stems of apple originated in the outer phloem (Dermen, 1948, 1951a, 1955). In the stem section of the 2–4–2 chimeral twig (Fig. 2-B), the phloem, derived from diploid L-III, is diploid. From such a twig, only diploid endogenous buds can arise. If a shoot is constituted as a 2–4–4 chimera, only tetraploid endogenous buds can arise from it (Dermen, 1955). When both diploid and tetraploid shoots develop from two separate buds on a stem situated at different points of the stem circumference as shown in Fig. 1 (buds *a* and *d*), it would indicate that in one part of such a stem the phloem is tetraploid and in another part it is diploid. This is illustrated diagrammatically in Fig. 2-B. The dotted line in this figure was drawn to indicate that often part of the stele in the stem may arise from L-II. This was shown to occur in cranberry (fig. 16, 18, Dermen, 1947) and in peach (fig. 11, 12, Dermen, 1953). Similar developments were observed in apple stems but because of lack of good preparations for illustration, they are not shown. The development of diploid and tetraploid shoots from endogenous buds on the same plant is evidence that a condition similar to that in the cranberry and peach was present in the tree shown in Fig. 1. Such a cytochimeral makeup may have been similar to that indicated in Fig. 2-B in which case it is assumed that growth from L-II in the stem had extended in part to the solid ink line and in part to the dotted ink line. Thus a shoot developed from an endogenous bud originating in the phloem in the area bounded by the dotted line would have been tetraploid and one from a bud in the phloem in the rest of the stele would have been diploid.

SUMMARY

A large-fruited sport of var. 'McIntosh' apple, 'Kimball Giant McIntosh' was reported earlier to have the 2–4–4 constitution. This conclusion was based on a study of one tree propagated from the mother sport tree. When some sister trees propagated from the sport tree were used to produce endogenous shoots, some of the endogenous shoots were diploid and one shoot was tetraploid, indicating that originally the sporting in the mother tree must have been to the 2–4–2 form. The present study shows this to be the case and that the 2–4–4 condition must have represented a derived form from the 2–4–2 type.

LITERATURE CITED

DERMEN, HAIG. *Periclinal cytochimeras and histogenesis in cranberry.* Amer. Journ. Bot. **34**: 32–43. 1947.

———. *Chimeral apple sports and their propagation through adventitious buds.* Journ. Hered. **39**: 235–242. 1948.

———. *Tetraploid and diploid adventitious shoots from a giant sport of McIntosh apple.* Journ. Hered. **42**: 144–149. 1951a.

———. *Ontogeny of tissues in stem and leaf of cytochimeral apples.* Amer. Journ. Bot. **38**: 753–760. 1951b.

———. *Periclinal cytochimeras and origin of tissues in stem and leaf of peach.* Amer. Journ. Bot. **40**: 154–168. 1953.

———. *Three additional endogenous tetraploids from giant apple sports.* Amer. Journ. Bot. In press.

——— and DARROW, G. M. *A tetraploid sport of McIntosh apple.* Journ. Hered. **39**: 17. 1948.

MAMMALOGY.—*A new subspecies of wood rat from Nayarit, Mexico, with new name-combinations for the* Neotoma mexicana *group.* E. RAYMOND HALL, University of Kansas Museum of Natural History.

(Received July 29, 1955)

At lower elevations on the west coast of the Republic of Mexico the big, rich brown, dark-tailed rodent *Neotoma* (*Hodomys*) *alleni* is the common wood rat. Nevertheless, *Neotoma mexicana* also occurs there in lesser numbers. At the lower elevations, individuals of *N. mexicana* are small. Smallness may be a response to warmth; anyhow *Neotoma mexicana* tends to be smaller in southern than in northern localities. Specimens from the coast of Nayarit pertain to an unnamed subspecies, which may be named and described as follows:

Neotoma mexicana eremita, n. subsp.

Type.—Female, adult, skin with skull and body-skeleton, no. 64532 KU; 1 mile south of San Francisco, 50 feet, Nayarit; January 27, 1955; obtained by J. R. Alcorn; original no. 17830.

Range.—Known only from the type locality.

Diagnosis.—Smallest-skulled of the subspecies of *Neotoma mexicana*; dark grayish to dull ochraceous above.

Comparisons.—From *N. m. parvidens*, *N. m. eremita* differs in smaller average size, less ochraceous upper parts, and less whitish (more plumbeous) underparts. *N. m. eremita* is less ochraceous even than the larger, geographically adjacent, *N. m. tenuicauda*.

Remarks.—The holotype of this small, dull-colored, rat, judged by the height of the crowns of the upper molariform teeth, is slightly younger than the holotype (71586 USNM) of *parvidens* and slightly older than the holotype (33594/45629 USNM) of *tenuicauda*. All three are females. Among named kinds of *Neotoma*, *N. m. eremita* resembles *N. m. parvidens* more closely than any other.

Measurements.—The holotypes of *eremita*, *parvidens* and *tenuicauda*, in that order, yield measurements (in millimeters) as follows: Occipitonasal length, 39.0, 41.5, 41.7; basilar length, 31.6, 32.3, 33.7; zygomatic breadth, 19.7, 20.6, ——; mastoid breadth, 15.0, 15.2, 15.8; interorbital breadth, 4.8, 5.3, 5.4; length of nasals, 15.6, 15.5, 15.4; length of incisive foramina, 8.5, 8.6, 8.9; length of palatal bridge, 7.0, 7.3, 7.6; alveolar length of upper molar series, 7.2, 7.9, 8.9; total length, 301, 295, 340; length of tail, 142, 141, 160; length of hind foot, 30, 31, 31.

Specimens examined.—Two from the type locality.

With assistance from the National Science Foundation, the Kansas University Endowment Association, and Alford J. Robinson, the Museum of Natural History of the University of Kansas has accumulated specimens of related kinds of wood rats, for example of the nominal species *Neotoma distincta* Bangs, *Neotoma navus* Merriam, and *Neotoma torquata* Ward as well as specimens of most subspecies of *Neotoma ferruginea* Tomes and *Neotoma mexicana* Baird. Examination of these specimens and also of those in the United States National Museum including those of *Neotoma tropicalis* Goldman gives basis for arranging all those mentioned above in this paragraph as subspecies of one species for which the oldest available name is *Neotoma mexicana* Baird 1855.

For example, specimen no. 63079 KU, here referred to *parvidens*, from 1 mile NNW of Soledad (approximately 30 km north of Punto Ángel), 4,700 feet, Oaxaca, is structurally as well as geographically intermediate between *N. parvidens* and *N. f. isthmica* Goldman and is regarded as an intergrade. Of 11 specimens examined of *N. navus* from southeastern Coahuila some have tails as short as *N. m. inornata* Goldman, the kind next adjacent to the north, and the expansion posteriorly of the frontals (not conspicuous in all specimens) occurs in some other subspecies of *N. mexicana* and leads to the conclusion that *N. navus* is only subspecifically different from *Neotoma mexicana inornata*. The differences between *N. tropicalis* and *N. f. isthmica* are of no

greater degree than are the differences between some other pairs of subspecies that are known to intergrade—*N. m. tenuicauda* Merriam and *N. m. madrensis* Goldman for instance. It is supposed, therefore, that specimens from geographically appropriate localities will reveal that *N. tropicalis* does intergrade with *M. f. isthmica*. In fact, Dalquest (Journ. Washington Acad. Sci. **41:** 363. Nov. 14, 1951) indicated subspecific status under *Neotoma ferruginea* for *Neotoma distincta* and *Neotoma torquata*. Hooper (Occ. Pap. Mus. Zool. Univ. Michigan no. 565: 22. Mar. 31, 1955) concluded that *Neotoma mexicana* and *Neotoma ferruginea* were conspecific because he found intergradation between the two in specimens that he assigned to the subspecies *tenuicauda* and for which he used the name-combination *Neotoma mexicana tenuicauda*. He did not, however, implement his conclusion with name-combinations for the kinds (other than *tenuicauda*) affected. Doing this and doing the same thing for the other nominal species that study reveals are only subspecies reduces the number of species in what has been referred to as the *mexicana*-group from eight to two, namely to *Neotoma mexicana* and *Neotoma chrysomelas* J. A. Allen. I know of no intergrades between these last two.

Two other species thought by some students to belong in the *Neotoma mexicana* group are *Neotoma goldmani* Merriam, 1903, and *Neotoma angustapalata* Baker, 1951. Because of the resemblance of their bacula to those of *Neotoma albigula* it seems best in the present state of knowledge to assign *N. goldmani* and *N. angustapalata* to the *albigula*-group. Information on the baculum of *N. goldmani* has been published by Rainey and Baker (Univ. Kansas Publ., Mus. Nat. Hist., **7:** 623. June 10, 1955). The cleaned bacula of *N. angustapalata* that Keith R. Kelson has shown me are indistinguishable from those of *Neotoma albigula*, figured by Burt and Barkalow (Journ. Mamm. **23:** 291. Aug. 13, 1942).

The named kinds of the *mexicana* group of wood rats should stand as given below.

Neotoma mexicana atrata Burt.

1939. *Neotoma mexicana atrata* Burt, Occ. Pap. Mus. Zool. Univ. Michigan no. **400:** 1, March 1, type from 4 miles west of Carrizozo, Lincoln County, N. Mex. Known only from the type locality.

Neotoma mexicana bullata Merriam.

1894. *Neotoma mexicana bullata* Merriam, Proc. Biol. Soc. Washington **9:** 122, July 2, type from Santa Catalina Mountains, Pima County, Ariz. Known only from the type locality.

Neotoma mexicana chamula Goldman.

1909. *Neotoma ferruginea chamula* Goldman, Proc. Biol. Soc. Washington **22:** 141, June 25, type from mountains near San Cristóbal, 8,400 feet, Chiapas, México.

Marginal records.—Chiapas: type locality. Guatemala: Hda. Chancol, about 13 miles north of Huehuetenango (Goldman, 1910: 69); Volcán Santa María (Goodwin, 1934: 54).

Neotoma mexicana distincta Bangs.

1903. *Neotoma distincta* Bangs, Proc. Biol. Soc. Washington **16:** 89, June 25, type from Texolo [Teocelo, near Jalapa], Veracruz, Mexico. Known only from the type locality.

1951. *N[eotoma]. f[erruginea]. distincta*, Dalquest, Journ. Washington Acad. Sci. **41:** 363, November 14.

Neotoma mexicana eremita Hall.

1955. *Neotoma mexicana eremita* Hall, present paper, type from 1 mile south of San Francisco, 50 feet, Nayarit, México. Known only from the type locality.

Neotoma mexicana fallax Merriam.

1894. *Neotoma fallax* Merriam, Proc. Biol. Soc. Washington **9:** 123, July 2, type from Gold Hill, Boulder County, Colo.

1910. *Neotoma mexicana fallax*, Goldman, North Amer. Fauna no. **31:** 56, October 19.

Marginal records (Goldman, 1910: 57–58, unless otherwise noted).—Colorado: 5 miles southwest of Fort Collins; 3½ miles west of Loveland, 5030 feet (26762 KU); Colorado Springs. New Mexico: Coyote Creek, 8 miles north of Guadalupita; Santa Rosa; Capitan Mountains; 1 mile south of Ruidoso, 6,500 feet. (35183 KU); east side of Sierra Blanca Mountains (Dice, 1942: 206); Manzano Mountains (V. Bailey, 1932: 183); San Mateo Peak; Datil Mountains (V. Bailey, 1932: 184); Grant; 18 miles north, 1 mile east of Farmington, 6,000

feet (34817 KU). Colorado: Cortez (Cary, 1911: 117); 4 miles west, 2 miles south of Cahone, 7,000 feet (34792 KU); Bedrock (Warren, 1942: 214); 1 mile southwest of Gateway, 4,600 feet (34773 KU); 2½ miles south of Fruita, 4,600 feet (34772 KU); Salida (Cary, 1911: 117); type locality.

Neotoma mexicana ferruginea Tomes.

1862. *Neotoma ferruginea* Tomes, Proc. Zool. Soc. London, 1861, pt. 3, p. 282, April, type from Dueñas, Sacatepequez, Guatemala.

Marginal records.—Guatemala: San Lucas (Goodwin, 1934: 54); type locality.

Neotoma mexicana griseoventer Dalquest.

1951. *Neotoma ferruginea griseoventer* Dalquest, Journ. Washington Acad. Sci. **41:** 363, November 14, type from Xilitla, San Luis Potosí, México.

Marginal records.—San Luis Potosí: El Salto (Dalquest, 1951: 363); type locality.

Neotoma mexicana inopinata Goldman.

1933. *Neotoma mexicana inopinata* Goldman, Journ. Washington Acad. Sci. **23:** 471, October 15, type from Chuska Mountains, 8,800 feet, San Juan County, N. Mex.

Marginal records.—Utah: mouth Nigger Bill Canyon, east side of Colorado River, 4 miles above Moab Bridge, 3,995 feet (Durrant, 1952: 337). Colorado: Ashbaugh Ranch (Goldman, 1933: 472). New Mexico: Gallup (Goldman, 1933: 472); Zuñi Mountains (*ibid.*). Arizona: Canyon del Muerto and head Spruce Creek, 9,000 feet, Tunitcha Mountains (*ibid.*). Utah: War God Spring, Navajo Mountain (Durrant, 1952: 337).

Neotoma mexicana inornata Goldman.

1938. *Neotoma mexicana inornata* Goldman, Proc. Biol. Soc. Washington **51:** 60, March 18, type from Carmen Mountains, 6,100 feet, Coahuila, México. Known only from the type locality.

Neotoma mexicana isthmica Goldman.

1904. *Neotoma isthmica* Goldman, Proc. Biol. Soc. Washington **17:** 80, March 21, type from Huilotepec, 100 feet, 8 miles south of Tehuantepec, Oaxaca, México.

1910. *Neotoma ferruginea isthmica* Goldman, North Amer. Fauna no. 31: 71, October 19.

Marginal records (Goldman, 1910: 72).—Oaxaca: Coixtlahuaca. Chiapas: Teopisca; Canjob. Oaxaca: Juchitan; Puerto Ángel; Oaxaca.

Neotoma mexicana madrensis Goldman.

1905. *Neotoma mexicana madrensis* Goldman, Proc. Biol. Soc. Washington **18:** 31, February 2, type from Sierra Madre, 7,000 feet, near Guadalupe y Calvo, Chihuahua, México.

Marginal records (Goldman, 1910: 60, unless otherwise noted).—Chihuahua: Colonia Garcia; Pacheco; near Parral. Zacatecas: 4 miles east of Calabazal (Hooper, 1955: 22); Sierra de Valparaiso. Durango: El Salto; ¼ mile south of Revolcaderos (Hooper, 1955: 22); 1½ miles west of San Luis (*ibid.*). Chihuahua: type locality; Carimechi (Burt and Hooper, 1941: 7).

Neotoma mexicana mexicana Baird.

1855. *Neotoma mexicana* Baird, Proc. Acad. Nat. Sci. Philadelphia **7:** 333, April, type from [mts.] near Chihuahua, Chihuahua, México.

Marginal records (Goldman, 1910: 56, unless otherwise noted).—Arizona: Rincon Mountains; Cave Creek, Chiricahua Mountains (Cahalane, 1939: 435). New Mexico: Animas Mountains (*ibid.*); Guadalupe Mountains (V. Bailey, 1932: 182). Texas: Fort Davis; Paisano. Chihuahua: Santa Eulalia. Durango: La Cienega de las Vacas. Sonora (Burt, 1938: 65): Cuchita; Oposura.

Neotoma mexicana navus Merriam.

1903. *Neotoma navus* Merriam, Proc. Biol. Soc. Washington **16:** 47, March 19, type from Sierra Guadalupe, Coahuila, México.

Marginal records.—Coahuila: type locality; Diamante Pass, 8,500 feet, Sierra Guadalupe, 18 miles east, 3 miles north of Saltillo (36346 KU).

Neotoma mexicana ochracea Goldman.

1905. *Neotoma ferruginea ochracea* Goldman, Proc. Biol. Soc. Washington **18:** 30, February 2, type from Atemajac, 4,000 feet, near Guadalajara, Jalisco, México. Known only from the type locality.

Neotoma mexicana parvidens Goldman.

1904. *Neotoma parvidens* Goldman, Proc. Biol. Soc. Washington **17:** 81, March 21, type from Juquila, 5,000 feet, Oaxaca, México.

Marginal records.—Oaxaca: type locality;

1 mile NNW of Soledad [approx. 30 kilometers north of Punta Ángel], 4,700 feet (63079 KU).

Neotoma mexicana picta Goldman.

1904. *Neotoma picta* Goldman, Proc. Biol. Soc. Washington **17:** 79, March 21, type from mountains near Chilpancingo, 10,000 feet, Guerrero, México.

1910. *Neotoma ferruginea picta* Goldman, North Amer. Fauna no. **31:** 72, October 19.

Marginal records (Goldman, 1910: 73).—Guerrero: Omilteme; type locality. Oaxaca: mountains near Ozolotepec.

Neotoma mexicana pinetorum Merriam.

1893. *Neotoma pinetorum* Merriam, Proc. Biol. Soc. Washington **8:** 111, July 31, type from San Francisco Mountain, Coconino County, Ariz.

1910. *Neotoma mexicana pinetorum*, Goldman, North Amer. Fauna no. **31:** 58, October 19.

Marginal records (Goldman, 1910: 59, unless otherwise noted).—Arizona: south rim, Grand Canyon (V. Bailey, 1935: 16); type locality; Winona (226370 BS). New Mexico: 10 miles southwest of Quemado; 10 miles west of Chloride; Kingston. Arizona: Prieto Plateau (205483 BS); Bradshaw Mountains (215809 BS); Simmons (215529 BS); Pine Spring (202570 BS).

Neotoma mexicana scopulorum Finley.

1953. *Neotoma mexicana scopulorum* Finley, Univ. Kansas Publ., Mus. Nat. Hist. **5:** 529, August 15, type from 3 miles northwest of Higbee, 4,300 feet, Otero County, Colo.

Marginal records (Finley, 1953: 534).—Colorado: type locality; Two Buttes [the peak]. Oklahoma: Tesequite Canyon. New Mexico: Clayton; Sierra Grande; Oak Cañon, Raton Range. Colorado: Trinidad; 20 miles east of Walsenburg.

Neotoma mexicana sinaloae J. A. Allen.

1898. *Neotoma sinaloae* J. A. Allen, Bull. Amer. Mus. Nat. Hist. **10:** 149, April 12, type from Tatameles, Sinaloa, México.

1910. *Neotoma mexicana sinaloae*, Goldman, North Amer. Fauna no. **31:** 60, October 19.

Marginal records.—Sonora (Burt, 1938: 65): San Javier; Mira Sol. Durango: Chacala (Goldman, 1910: 61). Sinaloa: Chele (Hooper, 1955: 22); Mazatlan (Goldman, 1910: 61). Sonora: Camoa (Burt, 1938: 65).

Neotoma mexicana solitaria Goldman.

1905. *Neotoma ferruginea solitaria* Goldman, Proc. Biol. Soc. Washington **18:** 31, February 2, type from Nentón, 3,500 feet, Guatemala.

Marginal records.—Guatemala: type locality; Sacapulas (Goodwin, 1942: 170–171). Honduras: Cerro Puca (*ibid.*).

Neotoma mexicana tenuicauda Merriam.

1892. *Neotoma tenuicauda* Merriam, Proc. Biol. Soc. Washington **7:** 169, September 29, type from north slope El Nevada de Colima, 12,000 feet, Jalisco, México.

1955. *Neotoma mexicana tenuicauda*, Hooper, Occ. Pap. Mus. Zool. Univ. Michigan no. **565:** 22, March 31.

Marginal records (Goldman, 1910: 74, unless otherwise noted).—Jalisco: mountains about 10 miles north of Bolaños. Zacatecas: Plateado. Aguascalientes: Sierra Fría (Hooper, 1955: 22). Jalisco: 2 miles NNW of Magdalena (*ibid.*). Michoacán: Zamora; 9 miles southeast of Pátzcuaro, 8,000 feet (Hall and Villa, 1949: 467): Tancítaro, 7,850 feet (*ibid.*). Jalisco: type locality; Talpa; San Sebastian.

Neotoma mexicana torquata Ward.

1891. *Neotoma torquata* Ward, Amer. Nat. **25:** 160, February, type from abandoned mine between Tetela del Volcán and Zacualpan, Morelos, México.

1894. *Neotoma fulviventer* Merriam, Proc. Soc. Washington **9:** 121, July 2, type from Toluca Valley, México, México.

1894. *Neotoma orizabae* Merriam, Proc. Biol. Soc. Washington **9:** 122, July 2, type from Volcán de Orizaba, Puebla, México.

1951. *N[eotoma]. f[erruginea]. torquata*, Dalquest, Journ. Washington Acad. Sci. **41:** 363, November 14.

Marginal records. — Hidalgo: Encarnación (Goldman, 1910: 64). Veracruz: 3 km east of Las Vigas, 8,000 feet (19840 KU). Puebla: Tehuacán, 1,700 m (Hooper, 1947: 55). Morelos: 2 km south of Jonacatepec (Davis and Russell, 1954: 77). México: north slope of Volcán Toluca (Goldman, 1910: 64).

Neotoma mexicana tropicalis Goldman.

1904. *Neotoma tropicalis* Goldman, Proc. Biol. Soc. Washington **17:** 81, March 21, type from Totontepec, 6,500 feet, Oaxaca. Known only from the type locality.

Neotoma mexicana vulcani Sanborn.

1935. *Neotoma ferruginea vulcani* Sanborn, Field Mus. Nat. Hist. Publ. 340, zool. ser., **20** (11): 84, May 15, type from south slope of Volcán Tajumulco, San Marcos, 13,200 feet, Guatemala. Known only from the type locality.

Neotoma chrysomelas J. A. Allen.

1908. *Neotoma chrysomelas* J. A. Allen, Bull. Amer. Mus. Nat. Hist. **24:** 653, October 13, type from Matagalpa, Matagalpa, Nicaragua.

Marginal records.—Honduras (Goodwin, 1942: 171): Montana Vasquez; Hatillo. Nicaragua: type locality.

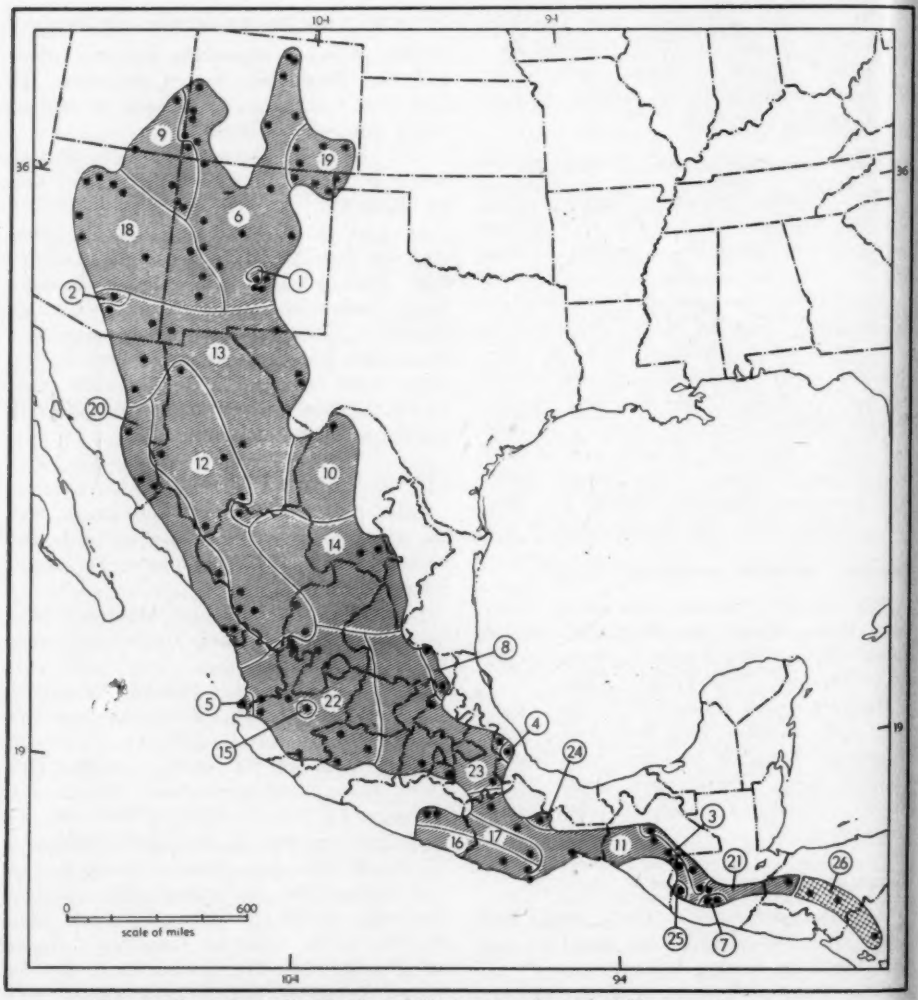


FIG. 1.—Geographic distribution of *Neotoma mexicana* and *Neotoma chrysomelas*

GUIDE TO KINDS:

1. *Neotoma m. atrata* Burt.
2. *Neotoma m. bullata* Merriam.
3. *Neotoma m. chamula* Goldman.
4. *Neotoma m. distincta* Bangs.
5. *Neotoma m. eremita* Hall.
6. *Neotoma m. fallax* Merriam.
7. *Neotoma m. ferruginea* Tomes.
8. *Neotoma m. griseoventer* Dalquest.
9. *Neotoma m. inopinata* Goldman.
10. *Neotoma m. inornata* Goldman.
11. *Neotoma m. isthmica* Goldman.
12. *Neotoma m. madrensis* Goldman.
13. *Neotoma m. mexicana* Baird.
14. *Neotoma m. navus* Merriam.
15. *Neotoma m. ochracea* Goldman.
16. *Neotoma m. parvidens* Goldman.
17. *Neotoma m. picta* Goldman.
18. *Neotoma m. pinetorum* Merriam.
19. *Neotoma m. scopulorum* Finley.
20. *Neotoma m. sinaloae* J. A. Allen.
21. *Neotoma m. solitaria* Goldman.
22. *Neotoma m. tenuicauda* Merriam.
23. *Neotoma m. torquata* Ward.
24. *Neotoma m. tropicalis* Goldman.
25. *Neotoma m. vulcani* Sanborn.
26. *Neotoma chrysomelas* J. A. Allen.